Kartongin venyvyyden parantaminen muokkaamalla kuitu-kuitusidoksia lujuusaineiden avulla

Tiivistelmä

Uusiutuvien ja muovinkaltaisten pakkausmateriaalien kysyntä on kasvamassa fossiilisten luonnonvarojen vähentyessä. Kartonki on uusiutuva materiaali mutta sen haittana on alhainen venyvyys toisin sanoen huono muokattavuus. Kartongin ominaisuudet tiedetään yleisesti hyvin koska niitä on tutkittu paljon. Kartongin venyvyys on kuitenkin yksi sen vähemmän tutkittu ominaisuus. Tässä työssä hypotetisoitiin, että kartongin tasomurtovenymää voidaan kasvattaa lisäämällä sen tasovetolujuutta muokkaamalla kuitu-kuitusidoksia lujuuspolymeerien avulla. Yhteensä 17 eri luonnosta löytyvää ja synteettistä lujuuspolymeeriä sekä kuusi näiden erilaista yhdistelmää testattiin. Tässä työssä tehtiin perinteisiä kartonkiarkkeja yksi- ja vaiheittaisesti kaksikerrospolymeroiduista kuiduista ja mitattiin kartonkiarkkien vetolujuus, murtovenymä, betaformaatio, neliömassa ja paksuus 50%:n suhteellisessa kosteudessa ja osittain 80%:n suhteellisessa kosteudessa.

Yksikerrospolymeroinnilla ainoa polymeeri joka merkittävästi kasvatti kartonkiarkin tasomurtovenymää molemmissa suhteellisissa kosteuksissa oli GPAM annoksella 10 kg/t. Mikään testatuista luonnonpolymeereistä ei merkittävästi kasvattanut tasomurtovenymää eikä tasovetolujuutta. Pienennetyllä sellususpension tilavuudella toisin sanoen korotetulla sakeudella tehdyt kokeet käyttäen kationista tärkkiä indikoivat, että yli 50 kg/t annos ja/tai matalampi sellususpension tilavuus ja/tai korkeampi sakeus voivat olla tarpeen kartonkiarkin tasomurtovenymän kasvattamiseksi merkittävästi. Kuitujen vaiheittaisella kaksikerrospolymeroinnilla, GPAM yhdessä CMC:n kanssa (75% + 25%) 10 kg/t annoksella oli ainoa polymeeriyhdistelmä joka tuotti merkittävästi referenssi polymeeriä, kationista tärkkiä (50 kg/t), korkeamman tasomurtovenymän kartonkiarkkiin. Vaiheittainen kuitujen polymerointi GPAM + CMC ja CPAM + CMC polymeeriyhdistelmillä kartonkiarkin vetolujuuden ja murtovenymän välillä oli 0.935 – 0.999 suuruinen parabolinen korrelaatio 80%:n suhteellisessa kosteudessa. Tämä tulos indikoi, että kartonkiarkin tasovenyvyyttä voidaan kasvattaa

lisäämällä sen tasovetolujuutta valituissa olosuhteissa kuten hypotetisoitiin. Lisäkokeita tarvitaan kuitenkin näiden indikaatioiden vahvistamiseksi tieteellisessä mielessä.

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Modification of paperboard sheet extensibility by inter-fiber bonding and strength agents

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Advisors	**Sr. Principal Scientist Jonni Ahlgren and Sr. Research Scientist Tom Lundin**

Modification of paperboard sheet extensibility by inter-fiber bonding and strength agents

Abstract

The demand for renewable and plastic-like packaging materials is increasing with the reduction of fossil resources. Paperboard is a renewable material but it suffers from limited extensibility, i.e., plasticity. The properties of paperboard are well-known and widely-studied topics. Extensibility and its improvement, however, have not been studied extensively. It was hypothesized in this work that the extensibility of paperboard hand sheet in terms of its in-plane breakage strain can be increased by increasing the in-plane tensile strength with the modification of inter-fiber bonding using polymeric strength additives. 17 different kinds of natural and synthetic polymeric strength additives and six combinations of these were tested. Polymer mono-layering and sequential polymer bi-layering techniques were tested to determine their effects on hand sheet properties such as tensile strength, strain at breakage, beta-formation, grammage and thickness at 50% and partly at 80% RH.

Applying a mono-layer technique, the only polymer that significantly increased the in-plane breakage strain at both RH was GPAM when dosed 10 kg/t. None of the natural polymers that were tested was able significantly to increase either the in-plane breakage strain or the tensile strength. Tests with a lower furnish volume and a higher furnish consistency in sheet formation using cationic starch indicated that dosages higher than 50 kg/t and/or a higher furnish consistency and/or a lower furnish volume could be needed to significantly increase the in-plane breakage strain of paperboard. When a sequential bi-layering technique was applied, GPAM with CMC (75%+25%) at a total dosage of 10 kg/t was the only combination that showed a significantly higher in-plane breakage of paperboard hand sheet than did the reference, cationic starch (50 kg/t). There was a parabolic correlation of 0.935 to 0.999 between the tensile strength and breakage strain of paperboard sheets prepared by the sequential bi-layering of GPAM + CMC and CPAM + CMC at 80% RH. This result indicates that the extensibility of paperboard can be increased by increasing its tensile strength under selected conditions, as was hypothesized. However, further experiments are needed to scientifically validate these indications.

Keywords: paperboard, cellulose fiber, breakage strain, extensibility, bonding, plastic deformation

Preface

This thesis was done for Kemira Oyj as a part of a larger cooperation project named the ACel (Advanced cellulose products) project. The work for this thesis was carried out in Kemira's Espoo R&D center during the year 2016. I would like thank my supervisor Professor Thaddeus Maloney from Aalto University and my advisors from Kemira R&D, Sr. Principal Scientist Jonni Ahlgren and Sr. Research Scientist Tom Lundin, for their guidance. Additionally, I would like to thank all the other Kemira scientists and managers who supported me during my work. I also wish to thank all the Kemira people in the laboratories for their help and patience. I feel that I am privileged and grateful for having the opportunity to work with these people.

Espoo, August 2016

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List of abbreviations

2D	Two-dimensional
3D	Three-dimensional
C2-C3	Covalent bond between second and third carbon of glucose
CD	Cross-Direction
CMC	Carboxymethyl cellulose
COD	Chemical oxygen demand
CPAM	Cationic polyacrylamide
DS	Dry Solids
HCLC	High- and Low-consistency mechanical treatment
HMW	High molecular weight
ISO	International Organization for Standardization
LC	Low Consistency
LMW	Low molecular weight
MG	Machine-glazed paper
MD	Machine Direction
NFC	Nanofibrillated cellulose
PAAE	Poly(amineamide) epichlorohydrin
PEC	Polyelectrolyte complexes
PEM	Polyelectrolyte multi-layering
RBA	Relative Bonded Area
SBS	Specific bond strength
S1	Outer layer of the secondary cell wall

S2	Middle layer of the secondary cell wall
S3	Inner layer of the secondary cell wall
SR	Shopper-Riegler
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl mediated oxidation of cellulose
TOC	Total organic carbon
V	Viscosity

1. Introduction

Paper and board have been manufactured and used for writing and packaging for thousands of years /1, p. 35; 36, pp. 62-75/. The use of paper for these purposes has continued to increase despite the increasing use of digital information and plastic derived from fossil hydrocarbons as packaging materials. During the last two decades digitalization has significantly reduced the demand for writing and printing paper. This has spurred the search for new fiber- and paper-based products. Moreover, the rapidly-decreasing fossil hydrocarbon resources, such as crude oil, and the global problems caused by the extensive use of these have prompted research into new non-fossil-based formable packaging materials. These driving forces, together with the fact that paperboard is a renewable resource, as well as its viscoelastic-plastic nature combined with its good strength properties, make fiber and paperboard potential raw materials for the production of formable packaging materials. However, since dry paperboard is relatively brittle in comparison with plastic, it suffers from limited extensibility, i.e., elastic and plastic deformation. Currently, the most widely used polymeric additive for strengthening paperboard is cationic starch. While this additive significantly increases the strength, it is only able to raise the extensibility of paper in terms of its tensile strain by a few percent, leaving the paper still relatively brittle /2,3/. Although the extensibility of paperboard as a molecular-level phenomenon is not clearly known, it is thought to be caused primarily by deformations within and between fibers and fibrils, i.e., the stretching and rearrangement of hydrogen bonds. Despite the lack of knowledge about molecular-level phenomena, the extensibility of paperboard correlates to some extent with easily measurable properties such as tensile strength and strain /8,11,29/. These properties have typically been determined using a tensile test, and the strength of paperboard has been an extensively researched area for several decades /4,5,6/. The extensibility of paperboard in terms of its strain at breakage can at best be increased by up to 15% by combining the refining of pulp with free (non-restraint) drying of the paper sheet /7/. However, extensibilities close to 10% achieved by various types of mechanical treatment inevitably cause significant losses in tensile strength /7,8/. An extensibility level that is not reachable by mechanical treatments is needed for formable packaging material applications /2,8/.

One promising approach to increase the extensibility of paperboard beyond traditional levels would be through the modification of the inter-fiber bonding by applying the correct combination of polymeric additives, either synthetic and/or (semi-)natural. Selecting the properties of the polymeric additive correctly in terms of optimal molecular weight and structure, charge density and distribution, polydispersity and/or the type and quality of functional groups would allow higher in-plane tensile strength and strain at breakage in paperboard. Although many studies have focused on increasing the strength of paperboard /3,21,35,73,74,**Error! Reference source not found.**,75,76,77/, few of these studies have focused on extensibility /66,67,68,69,70,71/. Even fewer studies have focused on the improvement of extensibility by the addition of polymeric additives /2,17/.

1.1 Objectives

The primary objective of this thesis was to determine the effects of various polymeric additives on the extensibility of paperboard, especially in terms of the in-plane breakage strain. A secondary objective was to achieve a broad understanding of inter-fiber bonding phenomena and their relation to the extensibility of paperboard.

The aim of this thesis was to increase the extensibility of paperboard by modifying fibers and fiber-fiber bonding with chemicals in aqueous media using polymeric additives. The extensive use of chemicals and additives in papermaking can significantly slow down or disturb drainage, web forming, drying and runnability, affecting the economics of paper production. However, these considerations remain beyond the scope of this thesis.

1.2 Hypothesis

In this thesis it was hypothesized that the extensibility of paperboard hand sheet in terms of its in-plane breakage strain can be increased by the modification of inter-fiber bonding with polymeric additives, causing an increase in the in-plane tensile strength.

2. Literature review

There is increasing demand for plastic-like, formable, renewable, biodegradable and recyclable packaging materials because of the limited and rapidly decreasing fossil carbon resources. Paperboard, which has a higher grammage than paper, fulfills three of these requirements but suffers from limited formability, i.e., extensibility. In order to increase the extensibility of paperboard it is necessary to understand all the factors and mechanisms involved. This literature review presents the theoretical background behind some of the relevant phenomena and concepts. The first section defines the extensibility and fundamental physical properties of paper materials. In the second section, all the known factors affecting the extensibility of paper are classified and described in more detail. The third section of the literature review discusses and justifies the modification of inter-fiber bonding with chemicals in terms of relevant modification methods and polymeric additives. The fourth section describes the most common polymeric additives used in papermaking and their potential for increasing the extensibility of paperboard.

2.1 Extensibility of paper-based materials

Paperboard is usually classified as a viscoelastic hierarchical composite material with a grammage above 80 g/m^2, consisting of cellulose, hemicellulose, lignin, fillers and additives in varying proportions. The extensibility of paperboard or any film-like material can be defined as its ability to increase its in-plane and/or out-of-plane length, thickness and/or width under a load until the point of failure. During extension, paperboard experiences tensile, shear and compressive forces, causing elastic and plastic deformations. Extensibility is often described as the in-plane strain at breakage and determined using a tensile test. The extensibility of typical paper grades, such as newsprint, copy, sack, bag or glassine paper, varies approximately between 1 and 6%, being about twice as high in the cross-machine direction as in the machine direction, expressed as strain from the original length /85, p. 13; 86, p. 2/. Currently, high-extensibility paperboard is utilized in two industrial-scale paper-forming processes, fixed blank and sliding blank processes, as can be seen from Figure 1. The fixed blank process can be further divided into air forming/vacuum forming, hydroforming and hot-pressing processes, while the sliding blank process can be classified into deep-drawing and stamping processes.

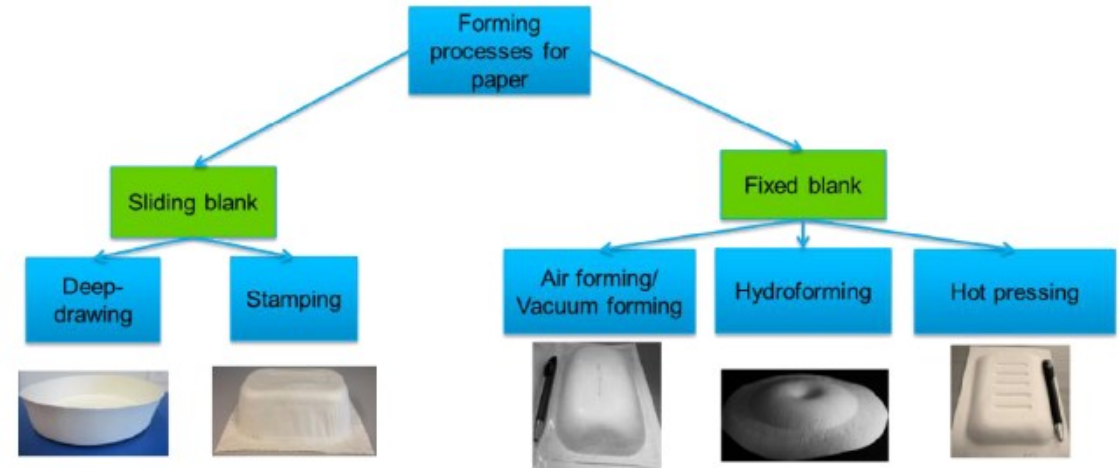


Figure 1. Classification of industrial paper-forming processes /2/.

Currently, only a few paper companies can produce paperboard grades suitable for deep-drawing requiring a breakage strain of about 20% /84/. According to the literature, a 20-30% breakage strain can be achieved by combining factors such as HC+LC – refining (High consistency + Low consistency), unrestrained drying, creping/compaction, suitable polymeric additives in the wet end, coating of the paper and moisture/temperature/strain rate control. In a recent study, Vishtal (2015) reported extensibility values of paperboard up to 30% to be possible by using agar and gelatin and combining unrestrained drying and compaction /2/. Companies currently supplying high-extensibility paper in commercial production include, e.g., Stora Enso, which produces Trayforma®, and BillerudKorsnäs, which produces FibreForm® products. Although the concept of thermoformable paperboards based on deep-drawing is rather old, it has recently attracted considerably increased research interest /2,17,79,80,81,82,83/.

2.1.1 Strength

One fundamental property of paper is strength, which can be defined as an ability to resist tensile, shear and compressional forces. Strength in paper is created by bonding between and within fibers and is governed by the relative bonded area (RBA), specific bond strength (SBS) and stress distribution within a bonded fiber network /64/. Inter-fiber bonding has been suggested to be the most important factor involved in the dry strength of paper /43/. The dry strength of paper is largely based on hydrogen bonding, whereas wet strength requires covalent bonds. In addition to mechanical treatments,

polymeric additives are typically used to increase the strength of paper. Several properties of polymeric additives, such as cationic charge or molecular weight, affect the strength of paper indirectly. However, the hydrophilicity of a polymeric additive has a strong direct correlation to the paper strength /60/.

Paper has several strength properties, such as burst, tensile, tear, compressional, interlayer and surface strength. These properties are measured using numerous methods, depending on the application using the paper or board. Strength property measurement methods differ in the direction, magnitude and/or duration of the force applied and the area under the force applied. Frequently, stiffness properties are also considered to be strength properties. Various strength properties of paperboard are described in Table *1* /3; 6, pp. 139-173/

Table 1. Strength property descriptors of paperboard /6, pp. 138-219; 23, pp. 1-18; 24, pp. 137-159/

Strength property	Generic definition
Burst strength	ability to tolerate pressure before rupture
Tensile strength	ability to resist rupture when a paper is under tensional force
Toughness (tensile energy absorption)	work done when the paperboard is stressed to rupture under tensional force
Folding endurance	durability to withstand repeatable folding
Internal bond strength (Z-directional strength, ply bond strength or transverse tensile strength)	ability to resist splitting/delamination under forces acting in the thickness direction
Interlayer strength (Scott bond strength)	ability to resist splitting/delamination under the plane directional forces
Compressibility	decrease in thickness after release of compressive force
Tear strength	ability to withstand tearing forces, i.e., high shear forces
Resiliency	ability to return to original thickness after the release of compressive forces
Bending flexibility	ability to bend before rupture under forces acting in the thickness direction, lack of stiffness
Elongation	ability to stretch until rupture under tensional force
Stiffness	ability to resist bending under a force perpendicular to the plane of the paperboard sheet
Softness	lack of hardness, opposite of hardness
Hardness	ability to resist indentation by some other material
Surface strength (IGT, pick and abrasion resistance)	ability to resist the pull-out of the coating layer from the paperboard surface

In the thermoforming processes, such as sliding blank, it can be assumed that tensile strength and elongation are the most significant strength properties. However, while sliding against the edge of the mold, paperboard also experiences compressional forces and thus requires a certain toughness, resiliency and compressibility. In the fixed blank processes such as air and hydro forming or hot pressing, the same strength properties are needed as in sliding blank processes but higher local elongation within paperboard can be assumed to take place as a result of the more uneven stress distribution. In order to avoid the formation of wrinkles, which is a typical challenge in the deep-drawing process, it is assumed that compressibility in the in-plane direction would be needed. /56, 61/

2.1.2 Elasticity

Generally, laboratory-made paperboard hand sheets can be assumed to have isotropic symmetries in-plane, with slight anisotropy in the z-direction as a result of the gradients in fiber length distribution, mainly because of fines. Machine-made paperboards are again different in the machine direction (MD) and in the cross-machine (CD) direction regarding their elasticity and other mechanical properties. The elasticity of any structured material, including paperboard, can usually be divided into linear and non-linear elasticity. Linear elasticity refers to the linear relation between the stress applied and the strain responses of the material under load. Linear elasticity or elastic strain is often defined by the point below which the deformation is reversible, i.e., the strain can reverse back to zero as the stress is released. In the case of paperboard, it is often difficult to define the true extent of the linear elasticity or elastic strain. This is because the relation between stress and strain starts to become non-linear and time-dependent slowly and gradually, i.e., there is no sudden change in the slope or tangent of the modulus for the stress-strain curve. Hence, other types of elasticities are described and mathematically modeled /62, 63/. One of them is hypoelasticity, which is defined by the linear relation between a time-dependent change in the stress and the deformation rate. Another type of elasticity is hyperelasticity, which includes linear elasticity and can also be non-linear. When hyperelastic material is under load the rate of change of the strain energy equals the rate of the work done by the stresses. It is not completely understood to what extent the elastic deformation is due to bond and/or fiber/fibril stretch and to

what extent it is due to hydrogen bond rearrangements, i.e., the breakage and reformation – slip – of the intermolecular bonding. Paperboard also has viscoelastic properties, which means that it dissipates energy irreversibly as heat upon stress release. The lost energy is due to the irrecoverable breakage and rearrangement of bonds as a viscoelastic material is under tension when it undergoes plastic deformations. The key difference between viscoelastic and elastic deformation is that in the former there is only partial recovery and in the latter full recovery to the original structure or dimensions after the release of stress /5, pp. 12-26; 6, pp. 139-150/.

When considering the extensibility of paperboard from the application point of view, as was done briefly in the first section of this chapter, it is permanent deformations that are required and therefore, one important parameter is the extent of the plastic deformation.

2.1.3 Plasticity

As the load increases the relation between the stress and strain of a paperboard, or any material in general, becomes non-linear and permanent deformation occurs upon the release of the stress. Deformation beyond this point is referred to as plasticity. The relation between elastic and plastic deformation in a typical overall deformation is depicted in Figure 2 for the case of a slightly creped paper.

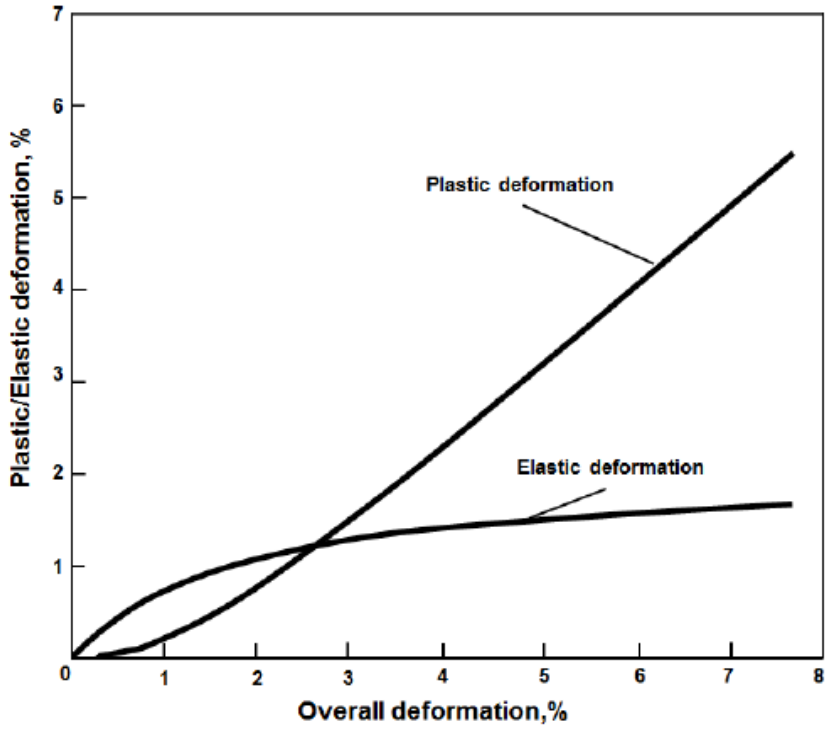


Figure 2. Share of elasticity and plasticity in overall tensile deformation of a slightly creped paper grade /11/.

As can be seen in Figure 2, it is the share of plasticity that governs the level of extensibility in paperboard above 3% overall deformation. The plasticity of a 2D paperboard structure can be divided into the plasticity of the fibers and inter-fiber bonds. The share arising from the fibers is usually larger than the deformation potential of the inter-fiber bonds. On the other hand, the plastic deformation potential of the inter-fiber bonding can be increased by multilayer polyelectrolyte adsorption /65,87/. The plastic behavior of paperboard under load can be modeled mathematically to some extent but highly accurate models are still lacking /91,93,94/.

The most commonly used paperboard strength additive is cationized starch having a branched 3D structure (amylopectin) and high molecular weight, which typically produces strong but relatively brittle paperboard with low plasticity. Thermoplastic starches have been developed and plasticity can be increased, although these products still suffer from moisture sensitivity /90,91/. The plasticity, as well as many other mechanical properties of a paperboard, is highly dependent on moisture, temperature and deformation time /95/. Chemicals such as glycerol, triacetin, citrates or glycol derivatives can be used as plasticizers or softeners in papermaking /88/. Plasticizers in paperboard adsorb moisture and disrupt hydrogen bonding, which allows fibers and fibrils to slide diffusively against each other. Good plasticizers usually have a low degree of polymerization but losses of strength are usually inevitable, as can be seen from Figure 3. A challenge in the creation of highly extensible paperboard, i.e., highly plastic paperboard, is how to maintain sufficient strength properties. Obviously, high extensibility is a compromise between strength properties and plasticity. A good compromise can probably be achieved by a combination of an additive with a suitable strength with a high molecular weight together with a plasticizer with a low molecular weight.

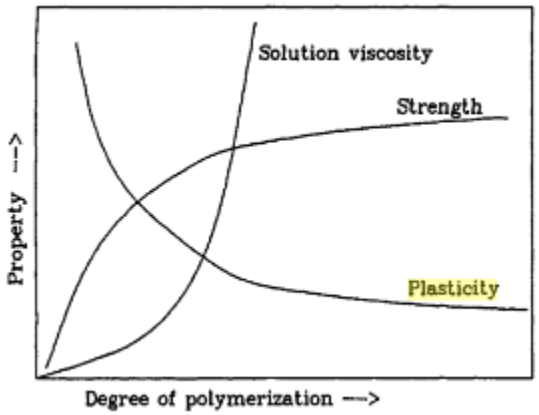


Figure 3. Plasticity and other properties as a function of average polymer DP /25, p. 402/

2.1.4 Load-elongation behavior of paper

When an increasing tensile load is applied to a paperboard structure, it starts to elongate or stretch at some point. During the elongation until rupture or breakage, the paper first undergoes relatively short elastic deformation, followed by viscoelastic deformation and finally plastic deformation as described above. The load-elongation behavior is often described using a stress-strain curve recorded during tensile tests, as can be seen from the data in Figure 4. From the stress-strain curve the ultimate tensile strength and maximum elongation can be seen; they can be found and calculated from the coordinates of the highest point of the curve. Other characteristics which can be determined from the stress-strain curve are the elastic modulus or Young's modulus, Poisson's ratio and yield strength. The elastic modulus is the slope of the linear part at the beginning of the stress-strain curve. Table 2 and 3 list some further parameters that can be calculated from stress-strain curve data if the true strains and specimen dimensions are known.

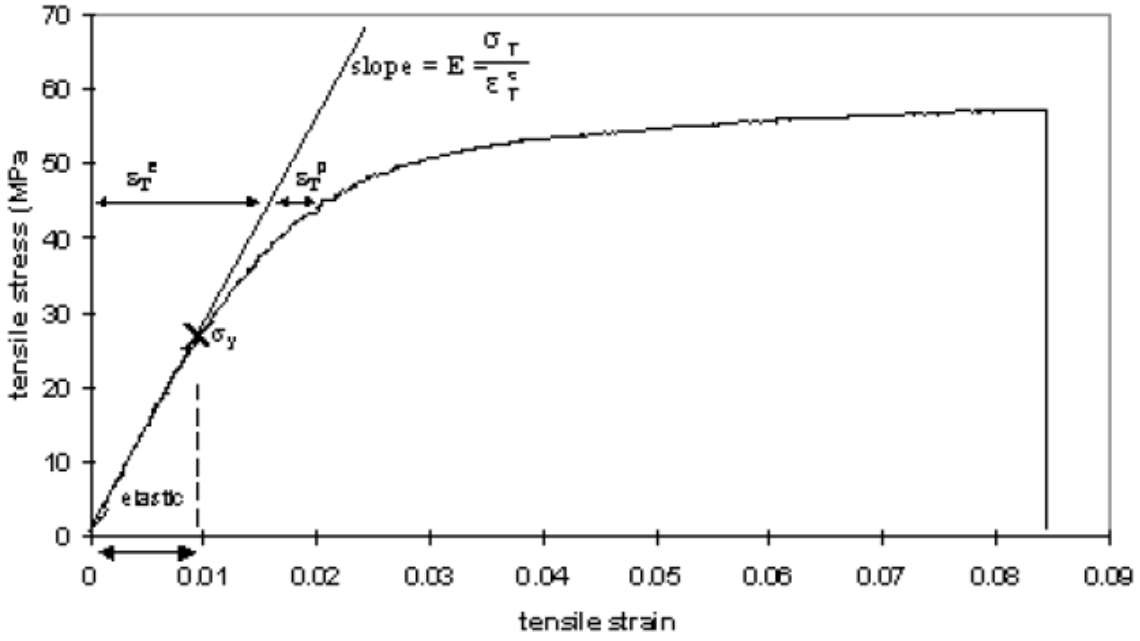


Figure 4. A typical stress-strain curve for a solid material /55/

Table 2. Calculation of elastic-plastic model parameters from the stress-strain data /55/.

True Stress	$\sigma_T = \frac{\sigma_T'}{(1 - \nu' \varepsilon_T')^2}$	(1)
True Strain	$\varepsilon_T = \ln(1 + \varepsilon_T')$	(2)
True Transverse Strain	$\varepsilon_t = \ln(1 + \varepsilon_t')$	(3)
Nominal Poisson's Ratio	$\nu' = -\frac{\varepsilon_t'}{\varepsilon_T'}$	(4)
Young's Modulus	$E = \frac{\sigma_T}{\varepsilon_T^e}$	(5)
True Poisson's Ratio	$\nu = -\frac{\varepsilon_t}{\varepsilon_T}$	(6)
True Plastic Strain	$\varepsilon_T^P = \varepsilon_T - \ln\left(1 + \frac{\sigma_T}{E}\right)$	(7)
True Transverse Plastic Strain	$\varepsilon_t^P = \varepsilon_t - \ln\left(1 - \nu' \frac{\sigma_T}{E}\right)$	(8)
True Plastic Poisson's Ratio	$\nu^P = -\frac{\varepsilon_t^P}{\varepsilon_T^P}$	(9)

Table 3. Symbols used in Equations 1-9 in Table 2.

$\sigma_T^{'}, \varepsilon_T^{'}, \varepsilon_t^{'}$	nominal (engineering) values of tensile stress, axial strain and transverse strain respectively, calculated using original specimen dimensions
$\sigma_T, \varepsilon_T, \varepsilon_t$	true values of tensile stress, axial strain and transverse strain respectively, these take into account the instantaneous specimen dimensions.
$E, \nu^{'}$	Young's modulus and nominal Poisson's ratio respectively. Modulus and Poisson's ratio values are calculated at a point or by regression over a strain range e.g. 0.0005 to 0.0025 strain range. The Young's modulus is calculated from stress divided by strain, and at small strains the true values are equivalent to the nominal values.
ν, ε_T^e	true Poisson's ratio and true elastic axial strain respectively
$\sigma_T^P, \varepsilon_T^P, \nu^P$	true axial plastic strain, true transverse plastic strain and true plastic Poisson's ratio respectively

The shape of the stress-strain or load-elongation curve will depend on numerous factors that were listed and described earlier in this chapter. Seth and Page discovered that factors such as the relative bonded area (RBA) and sheet density increased by beating do not affect the fundamental shape of the stress-strain curve but only the endpoint which indicates the maximum tensile strength and strain. This lack of a dependency is explained by the total drying shrinkage, which has been shown to have a linear relation with the tensile strength and strain at the point of breakage. Seth and Page concluded that the shape of the stress-strain curve is governed by fiber orientation and stress distribution. They also claimed that the viscoelastic part of the curve is governed by the properties of the fibers and the plastic part is governed by inter-fiber bonding. /28, 29/. On the basis of this observation, it can be assumed that a comparison of the true plastic strain values could be performed using Equation 7 from Table 2. Therefore, true plastic strain values could help when selecting the most potential polymeric additives for the improvement of the extensibility of paper.

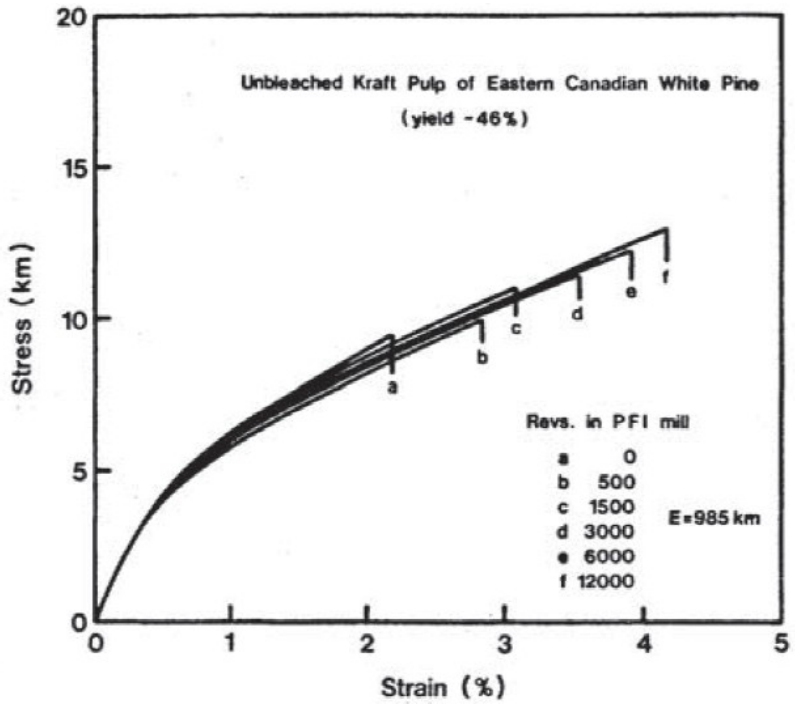


Figure 5. Stress-strain curves of hand sheet paper made from unbleached kraft pulp with different beating levels /29/.

In the case of an anisotropic composite material such as a paper or fabric, a biaxial tensile test is sometimes used /26/. Especially when the targeted property of a paper is high 3D extensibility, it might be reasonable to use biaxial tensile tests to evaluate the performance of the paper. On the other hand, a uniaxial tensile test is the most commonly used and standardized method for paper strength testing and might correlate sufficiently with the 2D and 3D formability of the paper. The data in Figure 6Figure 4 show how the uniaxial load-elongation behavior of a paper can vary between different grades and in different test directions. One of the key factors affecting the shape of a stress-strain curve in paper is the strain rate. There is some evidence that inter-fiber bonding is responsible for this time-dependent behavior of paper, but the challenge is how to measure bond stresses /96/.

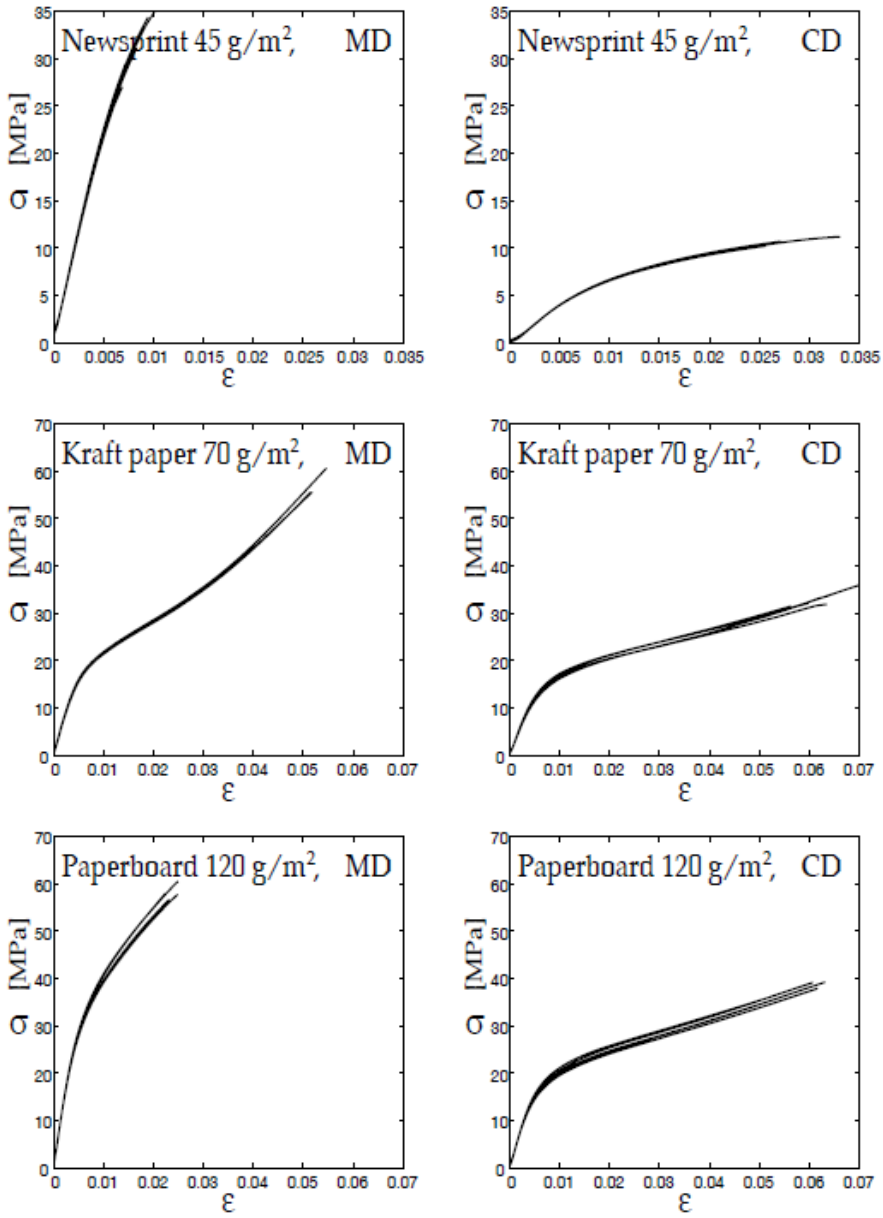


Figure 6. Stress-strain curves of typical newsprint, kraft paper and paper board in the machine (MD) and cross-machine directions (CD) /27/.

2.2 Classification of factors affecting paper extensibility

Generally, it can be stated that the maximum extensibility of paperboard is achieved when the full stretch potential of fibers, fibrils and the bonds between them is reached. The full stretch potential of fibers and fibrils cannot be reached unless the fibers are flexible enough, the bonding between them strong enough or the stress and strain distributions within the paperboard sheet are even. On the other hand, fibers and fibrils need to be strong enough in order to reach the full stretch potential of the bonds between them. /8/

Since paperboard is a relatively heterogeneous material in comparison with plastics, the distribution of stress and strain can be more important factors in some cases than the inter-fiber bonding. One proof of this was found by comparing networks with weak and strong bonds, which led to the conclusion that local strain concentrations are precursors of bond failures and not vice versa /57/. In addition, external factors such as humidity, temperature or strain rate have a tremendous effect on all of the properties mentioned above. Therefore, the factors affecting the extensibility of paperboard can be classified into four categories. These are the properties of fibers, structure of the fiber network, level of inter-fiber bonding and other external factors, as can be seen from Figure 7 /11/.

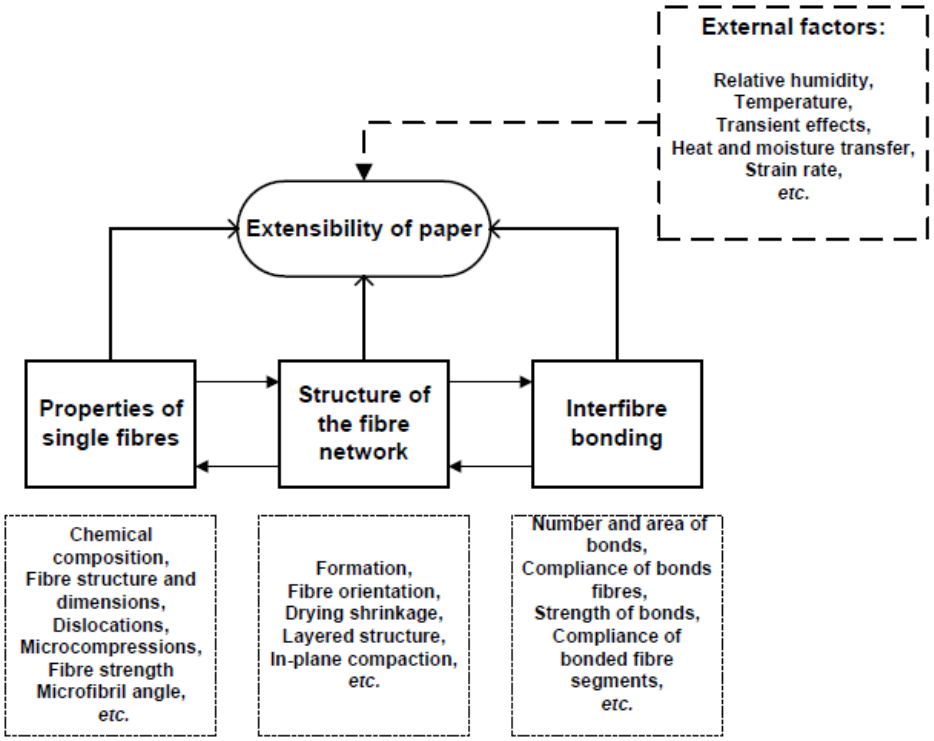


Figure 7. Classification of paper sheet extensibility factors /11/.

2.2.1 Properties of fibers

Wood fibers or the cells of a vascular plant resemble a complex 3D network of polysaccharides, lignin and proteins and consist of a thin primary cell wall and a thicker, three-layered secondary cell wall. The second layer of the secondary cell wall is significantly thicker than the other layers, and therefore dominates the mechanical properties of the fibers. The length and width of softwood fibers depend greatly on the species and growth period but the length is typically around 2-3 mm and the width ca.

30 µm. The range of the length is 1.4-7.2 mm and the width 20-65 µm. Hardwood fibers are typically around 1 mm long and about 20 µm in diameter, while hardwood fibers are 0.4-0.6 mm long and 1040 µm in diameter /30, p.18; 6, p. 57/.

Because of their better strength properties, the longer softwood fibers are often used for the production of packaging paper and board or as reinforcement fiber by mixing them with shorter hardwood or recycled fibers. If the bonds between the fibers are strong, the intrinsic fiber strength has a greater effect on the extensibility of the paper than the fiber length. Wood fibers in general can elongate by up to about 6% but even elongation of over 20% can be reached with some young softwood fibers /2, 98/.

Table 4. Average thickness and microfibril angle values of typical wood fibers /30, p.25/

Wall layer[a]	Thickness, µm	Number of microfibrillar layers (lamellae)	Average angle of microfibrils, degrees
P	0.05–0.1	-[b]	_[b]
S_1	0.1–0.3	3–6	50–70
S_2	1–8[c]	30–150[c]	5–30[d]
S_3	< 0.1	< 6	60–90
ML[e]	0.2–1.0	–	–

[a] *P primary cell wall, S_1 outer layer of the secondary wall, S_2 middle layer of the secondary wall, S_3 inner layer of the secondary wall, and ML middle lamella.*

[b] *Cellulose microfibrils form mainly an "irregular network".*

[c] *Varies greatly between earlywood (1-4 µm) and latewood (3-8 µm).*

[d] *The microfibrillar angle varies between 5° and 10° (latewood) and 20° and 30° (earlywood).*

[e] *An intercellular layer bonding the cells together. Contains mainly nonfibrillar material.*

The ultrastructure of the fibers, i.e., the cell wall layers in terms of thickness, number of microfibrillar layers and microfibrillar angle, varies significantly between and within plants, as can be seen from Figure 8 and Table 4. The microfibril angle in the layers S1 and S3 is sometimes perpendicular to the fiber axis /30; 30, p.25/. The higher the microfibril angle in the layer S2, the greater the applicable strain, as can be seen from Figure 9 /32/. Fibers with a high microfibril angle in the layer S2 in combination with suitable polymeric additives could be a useful approach for the production of extensible paper grades.

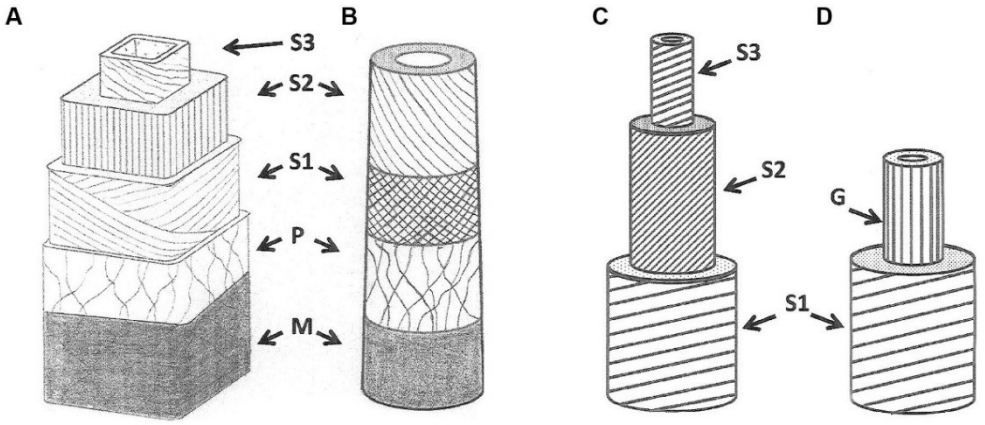


Figure 8. Normal and reaction wood cell wall structures in gymnosperms (A, B) and angiosperms (C, D). (A) Tracheid in normal wood, (B) tracheid in compression wood, (C) fiber in normal wood, (D) fiber in tension wood. G refers to the gelatinous layer /30/.

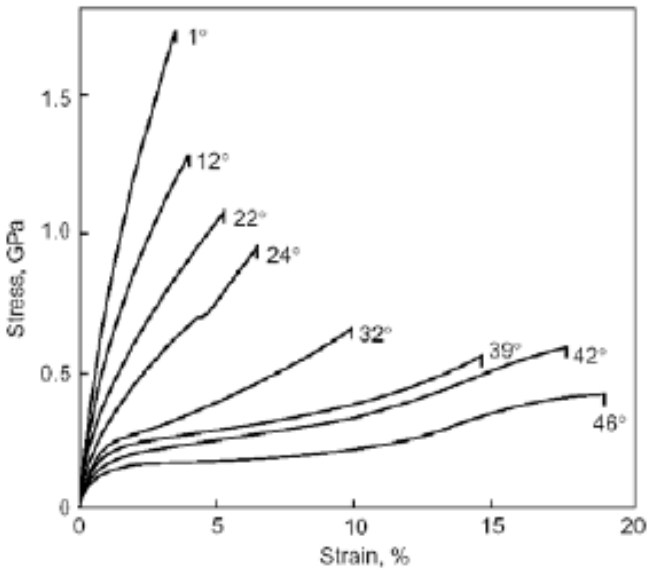


Figure 9. Effect of microfibril angle of S2 layer on load-elongation behavior of 45% yield black spruce fibers /32/.

As the fiber grows in nature it undergoes expansion by 10- to 100-fold compared to its original volume /13/. It is obvious that the outer layer, the primary cell wall, expands more than the inner layers. What is less obvious is that the outer layer will stretch more than the inner layers as the fiber grows. If the primary cell wall layer has a higher extensional capacity and the higher expansion during growth is not only due to biochemical reactions, it can be assumed that some part of the primary cell wall components could be potential additives to increase the extensibility of paper. However,

in the case of the mature cambial fibers used in paper making, the mechanism of fiber wall expansion is assumed to be somewhat different. One of the relatively abundant components in the primary cell wall of vascular plants is xyloglucan. Therefore, it is thought to be a crucial component in the enlargement of cell walls. However, the role of xyloglucan and other cell wall components remains unclear, as is which mechanisms contribute to cell wall extensibility or expansion in living and dead cells /18/.

Cellulosic papermaking fibers contain dislocations and micro-compressions, i.e., irregular regions which are mechanically weak points and have a significant effect on the strength properties of a paper. On the other hand, dislocations and micro-compressions are often the chemically most reactive points of fibers. These irregular regions are formed during the pulping process as the fibers are exposed to axial stresses and bending. Especially in refining or beating, the fibers are intentionally mechanically frothed against each other to produce dislocations, external fibrils and micro-compressions that provide increased tensile strength and strain. Micro-compressions in the inter-fiber bonds can also be formed during drying as a result of fiber contraction /97/. Therefore, it is difficult to say to what extent polymeric additives in the inter-fiber bonds change the mechanical properties of paper with respect to drying effects inducing micro-compressions. Different types of deformation affect the load-elongation behavior of a paper differently, as depicted in Figure 10. Reduced tensile strength is due to higher local stress concentrations, which again are due to the uneven stress distribution caused by differences in the straightening strain rates of curly and kinky fibers. /7,8,34/

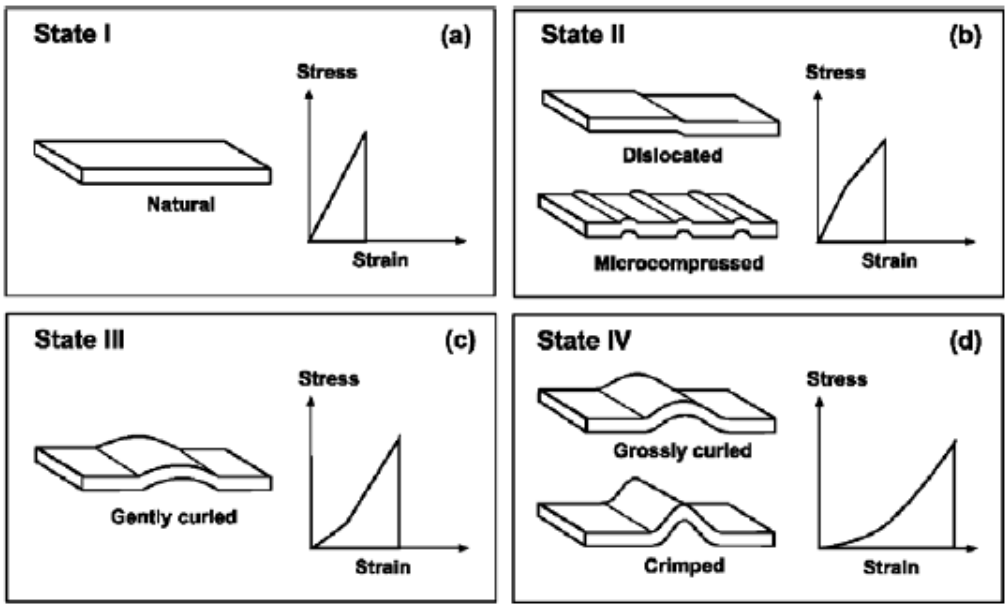


Figure 10. Effect of different deformation types of fibers on stress strain behavior of paper sheet /33/.

As the native cellulosic fibers are liberated inside wood chips while they are being delignified during pulping, the porosity of the fiber walls increases. The porosity is further increased in refining as a result of delamination and other dislocations. Increased porosity improves the swelling of the fibers, which in turn has a significant effect on fiber flexibility. Well-swollen and flexible fibers increase the overall compliance via their fiber-fiber contacts and relative bonded area, which are reflected as increased tensile strength and strain. The valency and species of the counter-ions attached onto anionic groups on fiber and fibril surfaces have significant effects on fiber swelling /35/. The intrinsic strength of fibers is difficult to measure because of their small size. An average measure of fiber strength can be performed via the zero-span tensile strength, although this cannot provide any strength metrics for individual fibers /34/.

2.2.2 Inter-fiber bonding properties

An inter-fiber bond describes the bonding zone, or area between two fibers that are close enough to show mutual adhesive forces keeping them together. Inter-fiber bonding properties include factors such as the molecular bond type and strength, the specific bond strength, the relative bonded area, the compliance of inter-fiber bonds, the number of inter-fiber bonds and the number of molecular (covalent) bonds.

2.2.2.1 Molecular bonding types

Cellulosic fibers are usually chemically modified by the formation of new and/or the cleavage of existing internal chemical bonds such as ionic, covalent and/or hydrogen bonds in order to increase hydrogen bonding sites, molecular weight and/or charge density. Other types of small-range molecular interactions such as van der Waals or simple mechanical locking are known to contribute to the fiber-fiber bonding properties but their contributive share is not known /41, pp. 24-33/. Generally, the molecular-level mechanism of the chemical modification of fibers on the extensibility of paper is not completely understood. It is commonly accepted that hydrogen bonds are primarily responsible for the mechanical properties of a paper by the formation of adhesive forces between cellulosic fibers. Allan et al. have suggested that adhesive inter-fiber forces are a result of ionic bonding /10/. Cellulosic fibers usually have a negative net surface charge, which is mostly caused by carboxylic groups of cellulose and uronic acid groups of hemicelluloses.

2.2.2.2 Number and strength of bonds

Inter-fiber bonds are mostly affected by shear forces, especially when paper is affected by tensional forces. This is due to the geometrical complexity of the fiber network, in which the direction of the inter-fiber bonding planes varies significantly and is rarely aligned perpendicular to the direction of the force, i.e., molecular bonds in a paper are rarely loaded under pure tension or compression. On the other hand, it is difficult to define and, especially, measure the direction of the force relative to the direction of an individual molecular bond or even the interfiber bonding plane, which makes the difference between tensional, compressional and shear forces. However, the interfiber bond strength defines the extent of the load that the bond can carry before the adhesive joint between the fibers disappears. The specific bond strength is defined as the ratio between the bond strength and area. The usefulness of the specific bond strength is questionable because the bonded area probably contains spots without molecular bonds and therefore, the bond strength is not always directly proportional to the bonded area. With image analysis methods it is possible to determine the number of inter-fiber bonds along the fiber /37/. Chemical bonds and van der Waals bond energies can be measured in terms of dissociation energies. The covalent, ionic, hydrogen and van der Waals bond dissociation energies are 436, 412, 20 and 3.9 kJ/mol, respectively /41, p. 25/. It is

generally believed that hydrogen bonds make the highest contribution to the energy of the inter-fiber bond. However, one of the latest research reports in this field states that the role of the van der Waals forces can be even more significant /99/.

2.2.2.3 Compliance and area of inter-fiber bond

In order to form an inter-fiber bond the surfaces of the fibers need to get close enough to one another. The distance between adjacent fiber surfaces has to be approximately less than 0.3 nm in order for hydrogen bonds to form. The surfaces at the inter-fiber bonds are rarely smooth enough to be perfectly bonded at the molecular level. This surface roughness or unevenness reduces the compliance of the inter-fiber bonds. The relative bonded area (RBA) is the total surface area of the inter-fiber bonds divided by the total surface area of the fibers. The fines and microfibrils produced in beating increase both the compliance and RBA by creating more surface area for the bonds, making the fibers more flexible, and by filling the cavities at the inter-fiber surfaces. The bonded area between fibers can be numerically estimated from the light scattering measurement or by image analysis. Figure 11 shows the optical bonded area which is not accessible for light scattering. The compliance of the bonded area in order to increase the amount of bonds can be improved, for example, by increasing the swelling of the fibers and/or the wet pressing force. The degree of fiber swelling can again be increased by changing the counter-ion of the anionic groups of cellulosic fibers from H^+ to Ca^{2+} or into the Na^+ form. Through the use of such approaches the bond strength between the fibers in paper can be increased by more than 100% /3; 6, pp. 24-26; 35, 37/.

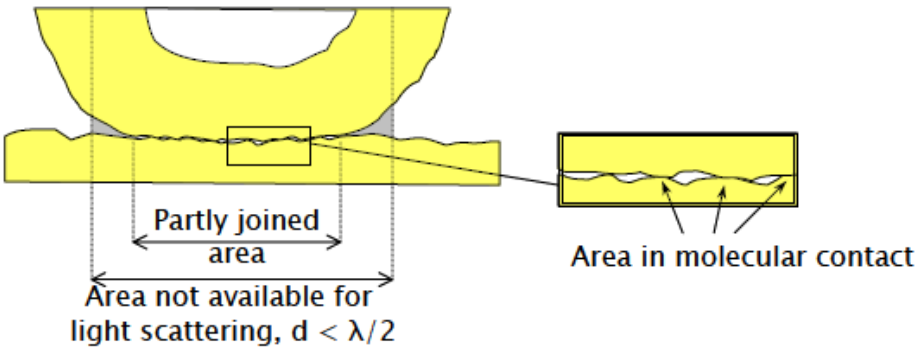


Figure 11. Visualization of the estimated optical and physical, partly molecular inter-fiber bond areas /3/.

2.2.3 Paper network properties

Paper networks consist of more or less randomly arranged cellulosic fibers in the in-plane direction connected to each other primarily by hydrogen bonds. A paper network does not have any particular structure because of the high degree of randomness. However, the structure can be defined statistically by some mean, deviation and probability values /39, 40/. Machine-made paper has a less random in-plane structure than laboratory-made hand sheet paper, mainly as a result of the moving wire in the paper machine. Paper network properties can be classified in many ways, such as 2D and 3D network geometry, fiber orientation, formation, drying shrinkage and in-plane compaction. In practice, paper is always three-dimensional, but many of its properties are explained by two-dimensional properties. One of the two-dimensional properties of a paper is coverage, which is the average number of fibers at any point of the paper plane. The average coverage can be calculated by dividing the basis weight of the paper by the basis weight of the fibers. Network connectivity in terms of the relative bonded area is another important 2D property which gives the average degree of bonding and can be determined from coverage. In three dimensions there are pores between fibers which affect many properties of the network. The pore size is dependent on properties of fibers such as type, width, length and flexibility. The pore size is naturally also dependent on the retention and distribution of additives and fillers, together with the press or calendar conditions that are applied. Smaller pore sizes increase the relative bonded area and density, which in turn affect the mechanical and optical properties of the paperboard. This is due to the fact that the dimensions of the fibers are usually greater than the thickness of a paperboard sheet, and hence the fibers are less randomly arranged in the thickness direction, i.e., the z-direction, than in the in-plane direction. This fact leads to a layered and/or felted structure of paper sheets. The structure of a paperboard sheet is usually more felted if high stock consistency is used, while it is more layered at lower consistencies. The web drainage rate and pulsation also affect the sheet structure /6, pp. 14-50/.

Moreover, the paper network structure is affected by formation phenomenon such as the stochastic landing of fibers, fillers and/or additives onto a wire or web. This leads to the uneven distribution of particles, i.e., variation in basis weight. Flocculation or aggregation of fibers, i.e., poor dispersion, leads to bad formation. A certain degree of

headbox turbulence in the wire section is needed for sufficient disruptions of flocs in order to achieve a good formation. Since formation is a measure of the variation in the basis weight it can be assumed that it has a significant effect on the distribution of the inter-fiber bonds. It is assumed that the distribution of the inter-fiber bonds affects the stress distribution within the paper sheet, which in turn will have significant effects on the tensile strength and strain at the point of breakage in a paperboard. Generally, poor formation causes significant variations in almost every paper property descriptor. Fiber orientation describes how fibers are aligned two- and three-dimensionally relative to each other and to the machine direction. As mentioned earlier, fibers are primarily oriented in the in-plane direction, less in the z-direction and more parallel in the machine direction than the cross-machine direction. The fiber orientation is closely related to anisotropy and is a strong function of almost every in-plane mechanical property of a paper. The orientation of the fibers is often expressed as the fiber orientation index or fiber orientation angle. The fiber orientation can be adjusted by varying the speed difference between the sprayed stock and wire. By varying the stock concentration and controlling the stock spraying, the orientation of the fibers can also be varied significantly /6, pp.14-50/.

In the drying of a wet paperboard web the majority of the free, unbound water is removed mechanically. The remaining free water, like most of water bound to hydroxyl groups of cellulose and hemicellulose, is removed by thermal energy. The surface tension of the water in the decreasing voids will pull fibers and fibrils closer to each other until the distance between the surfaces is only fractions of nanometers and molecular bonds, mainly hydrogen bonds, start forming. This phenomenon is called the drying shrinkage of paperboard and it can be affected by mechanically straining the paper web during drying. This so-called wet straining reduces the basis weight and changes the arrangement and shape of the fibers and can increase the final tensile strength to a certain extent, beyond which it can decline rapidly in the case of poor formation. Drying shrinkage has significant effects on the properties of paperboard. Increasing the drying shrinkage reduces the elastic modulus and tensile strength but increases the breaking strain proportionally /6, pp. 169-170/.

Wet pressing has a significant effect on the paper network structure. In-plane compaction reduces the porosity, i.e., it increases the sheet density, which provides a

higher relative bonded area of the paperboard. An increased relative bonded area usually improves the out-of-plane strength properties but can reduce the in-plane tensile strength and stiffness in some cases. Some compaction of a paperboard also takes place in calendaring but its significance for extensibility is lower. Wet pressing increases the bending of the fibers in thickness direction, i.e., the bending of the fibers against each other, which increases the extensibility of the paperboard in terms of breakage strain /6, pp. 81-83, 29/.

2.2.4 External factors

External factors such as the relative humidity/moisture and drying constraint of a paperboard and their historical variation have a great effect on the paperboard extensibility, as well as on all the other mechanical properties. Other significant external factors that affect the extensibility of paperboard are temperature, heat and moisture transfer, the rate of tension applied, changes in the rate of tension and specimen dimensions, as can be seen from Figure 12. /27/.

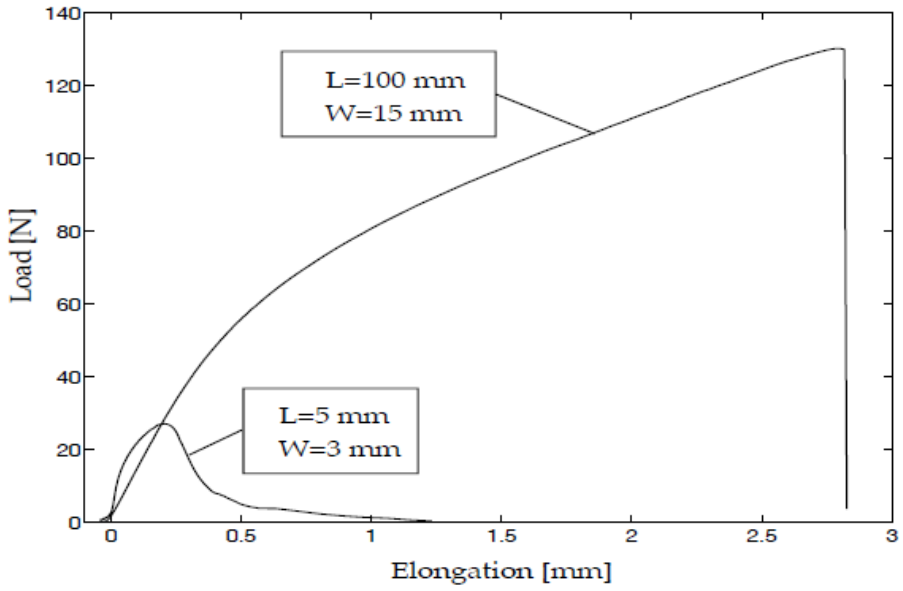


Figure 12. Stress-strain behavior of paperboard with a grammage of 120 g/m^2 /27/

Increasing the temperature induces the thermal movement of molecules on the cellulose fibrils, which tends to increase the distance between the fibrils. At some stage the increased distance may induce the breakage of hydrogen bonds and allow the fibrils to slide against each other. Water-induced hydrogen bonding breakage and the sliding of fibrils against each other take place when the moisture content of the paper is increased.

Both temperature and moisture increase the breakage strain and reduce the tensile strength of a paper to a certain extent, as can be seen from Figure 13.

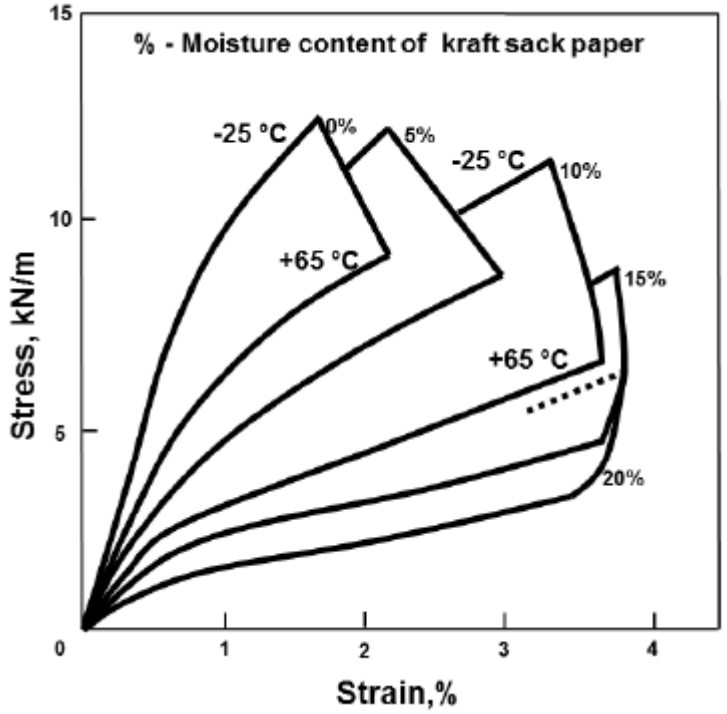


Figure 13. Stress-strain behavior of kraft sack paper under various moisture and temperature conditions. /3/

Mäkelä (2009) showed that the tensile stiffness, tensile strength, strain at break, and tensile energy absorption of the dried sheets have linear relationships with the total drying strain of the paper sheets. These relations were not dependent on the drying time, temperature or constraint history. However, the in-plane tensile properties and final drying stress had a non-linear relation with the total drying strain of the paper sheets and these relations were dependent on the drying constraint history to a great extent /28/.

Paperboard is a viscoelastic material. Hence, its stress-strain curve will depend on the rate of the strain applied. Increasing the strain rate of a paper increases its tensile strength and elastic modulus but usually causes losses in terms of its breakage strain. In the case of machine-glazed (MG) paper, the breakage strain is relatively independent of the rate of strain, as can be seen from Figure 14. The lower the rate of strain, the longer the time taken for the fiber network to relax and the paper to deform plastically.

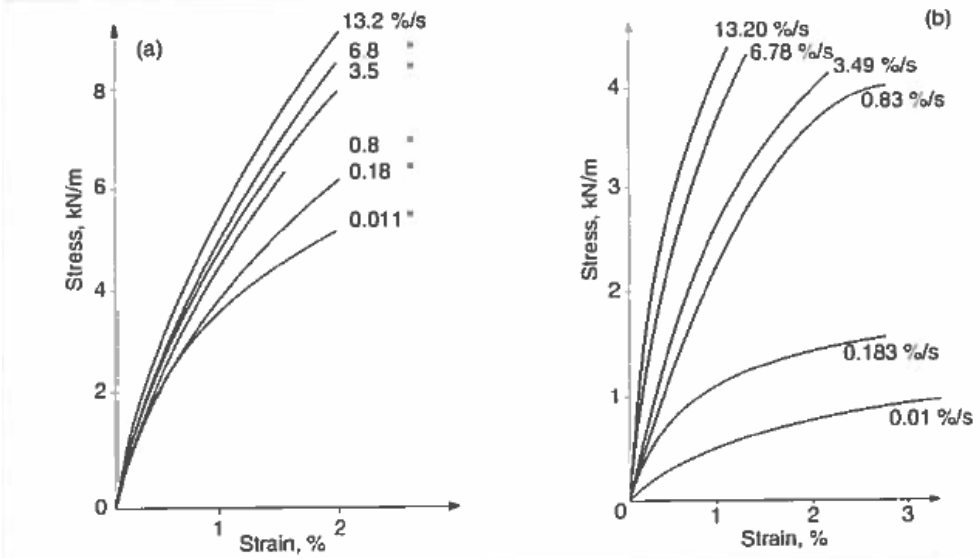


Figure 14. Effect of strain rate on stress-strain curve of a) MG paper and b) cellophane /6, p. 154/.

2.3 Chemical modification of inter-fiber bonding properties

The chemical modification of cellulosic fibers in the papermaking process can be carried out in stages before the pulp suspension is sprayed onto a wire, or for a wet paper web using some spraying, surface sizing or coating process. Stock preparation, as well as the whole papermaking process, takes place in an aqueous medium containing various amounts and types of dissolved and colloidal matter. In order to achieve good retention, formation, and runnability for a given paper quality, the physicochemical properties of the pulp suspension are adjusted and controlled prior to web forming. This is in terms of consistency, freeness, pH, conductivity, temperature, charge, air content, cation contents, COD/TOC, flow, etc. When selecting chemicals for the modification of fibers it should be considered that paper products should be easily recyclable, biodegradable and non-toxic. These factors, together with other papermaking parameters, are more or less interrelated to each other and this makes the chemical modification of fibers challenging and limits the selection of suitable chemicals and methods /36, pp. 174-178; 41, pp. 205-219/.

2.3.1 Modification methods

Chemical modification methods for cellulosic fibers can be classified in multiple ways on the basis of the reaction type, bonding type or functionality achieved. The methods used for the chemical modification of cellulosic fibers include etherification,

esterification, oxidation, cross-linking, graft-polymerization, mono-, bi- and multilayer polyelectrolyte adsorption and hydrophobization. Etherification, oxidation and esterification often require a non-aqueous reaction medium and costly and time-consuming process steps, and are therefore uncommon in industrial papermaking processes.

2.3.1.1 Adsorption

Adsorption is a surface phenomenon in which atoms, ions or molecules of liquid, gas or solids in suspension are attached to a surface by chemical bonds (chemisorption) or by short-range van der Waals forces (physisorption). The adsorption of water-soluble polyelectrolytes in the wet end is the most commonly used modification method for papermaking fibers. Polyelectrolytes are adsorbed onto the fibers by electrostatic forces caused by ionized groups. The presence of dissolved inorganic salts in a pulp furnish will increase the amount of adsorbed polyelectrolytes on the cellulosic fiber to a certain extent, which is usually around 1 to 10 mmol/L, depending on the charge density of the polyelectrolyte and other competing counterions /65/. After a certain degree of adsorption the surfaces of the particles in the pulp suspension become covered with adsorbent and the rest of the adsorbent ends up in the white water loop of the paper machine. In order to increase the adsorption of polymers on paper fibers a polyelectrolyte multi-layering technique (PEM) was developed in 1997 by Decher /89/. The adsorption of oppositely charged polyelectrolytes sequentially on cellulosic fibers as bi- or multilayers, i.e., the layer-by-layer technique or PEM, can significantly increase the strength and/or breakage strain of paper /19,58,59,65,89/. In this layer-by-layer technique, the first polyelectrolyte layer to be adsorbed on the fibers is typically cationic as a result of the anionic surface charge of the cellulosic fibers. Before the adsorption of the first layer impurities can be washed away from the fibers and/or the fibers can be further anionized prior to adsorption. The subsequent polyelectrolyte layers are alternating anionic and cationic ones. Polyelectrolyte adsorption on cellulosic fibers often enhances the swelling of the fibers, which in turn enhances the fiber flexibility. Increased flexibility provides a higher sheet density and larger relative bonded area, which have significant effects on the mechanical properties of the paper. Another way to adsorb oppositely charged polyelectrolytes on fibers is the adsorption of polyelectrolyte complexes (PEC), which are polyelectrolyte aggregates containing both

anionic and cationic polymers. The addition of polyelectrolytes prior to refining can significantly reduce the amount of energy needed to reach a certain tensile strength level in the paper. Gustafsson (2012) demonstrated that by layering unbeaten, once-dried softwood kraft fibers 10 times in a 10-Mm NaCl medium using PAH and hyaluronic acid sequentially in turn, it was possible to increase the tensile strength from 25 Nm/g to 70 Nm/g and the breakage strain from 2% to 6.5% /12, 15, 16, 51/.

2.3.1.2 Cross-linking

Cross-linking takes place by definition when two polymer chains are attached or linked to each other by a covalent or ionic bond. In practice, all polymeric additives commonly used in the papermaking industry are cross-linking agents and some of them, such as wet-strength resins, also cross-link themselves at higher addition levels. The most commonly used polymeric paper additive, cationic starch, forms ionic bonds between the carboxylic and uronic groups of cellulose and hemicellulose. Cross-linking by covalent bonding takes place, for example, when wet strength additives such as polyamine-epichlorohydrin or glyoxal-polyacrylamide-based polymers are used. The cross-linking agents used in paper coating are also called insolubilizers and their purpose is to increase the water resistance of fiber networks or reduce physical wetting. Starch can also be the polymer that is cross-linked, for example when glyoxal is used for curing the starch in the coating of a paper /22, 42, pp.122-123/.

2.3.1.3 Graft polymerization

Graft polymerization, i.e., grafting means the attachment of a polymer chain to another polymer from one end by covalent bonding. In order to form a covalent bond a relatively high amount of energy, time, non-polar reaction media and costly high-reactive chemicals are often needed, which limits the use of the grafting technology in papermaking. On the other hand, the extensive grafting of cellulose fibers could reduce the need for energy-intensive beating, which in turn could make grafting a feasible pretreatment for papermaking fibers /103/.

2.3.1.4 Other methods

Within a cellulose molecule its linear chain structure with glucosidic linkages combined with inter- and intra-chain hydrogen bonds makes the cellulose chain extremely stiff /72/. The hydrogen bonds induced between cellulose chains make the fibrils and fibers

stiff. A selective oxidation of certain covalent bonds of cellulose molecules also leads to the selective elimination of hydrogen bonds within and between cellulose chains. Some research results indicate that this type of selective oxidation method leads to reduced stiffness and significantly increased flexibility of fibers and paper made of these fibers. One example of this type of modification method is the selective oxidation of cellulose C2-C3 bonds. Sodium periodate was used as an oxidant, followed by reduction of the aldehydes that had formed with sodium borohydride. Bleached unbeaten softwood kraft fibers were oxidized with this method to a 27% degree of the conversion of the C2-C3 bonds. A tensile strength of 90 MPa and a strain at breakage of 11% were measured from restraint-dried hand sheets. With this treatment the tensile strength and strain at the breakage of the fibers also increased by about 100% /20/. Although there are some disadvantages reported for this kind of oxidation from the application point of view, the results still indicate the potential of this method for the production of extensible paper. By combining optimized refining and chemical modifications such as the selective oxidation of fibers together with polymeric additives, impregnation with plasticizers and an optimized drying method, paper with a breakage strain of at least 30% can be produced /56/.

2.4 Structure and properties of polymeric additives

This section covers conventional and non-conventional bio- and synthetic polymers suitable for papermaking. Their molecular structures and properties are discussed. Polymeric additives are traditionally used in papermaking to improve retention, drainage, formation, sizing, optical and strength properties. Over 50% of all the chemical additives used in papermaking are starch-based, about one third are synthetic polymers and the rest are aluminum derivatives and other products /42, pp. 62-64/. The effect of the structure and properties of a polymeric additive, such as its 3D structure, molecular weight and charge density, have a significant effect on the properties of the paperboard.

2.4.1 Biopolymers and their derivatives

Biopolymer is often used as a synonym for natural polymer and can be defined as polymeric substances composed of proteins, nucleid acids or polysaccharides produced by biological organisms /46/. Modified polysaccharides such as cationic starch and

carboxymethyl cellulose are currently the only biopolymers that have commercial importance in papermaking. Other potential biopolymeric papermaking additives include chitosan, made from chitin, vegetable gums, latex and hemicelluloses such as xyloglucan or glucomannan. The molecular structures of some potential papermaking biopolymers are shown in Figure 15 /21/.

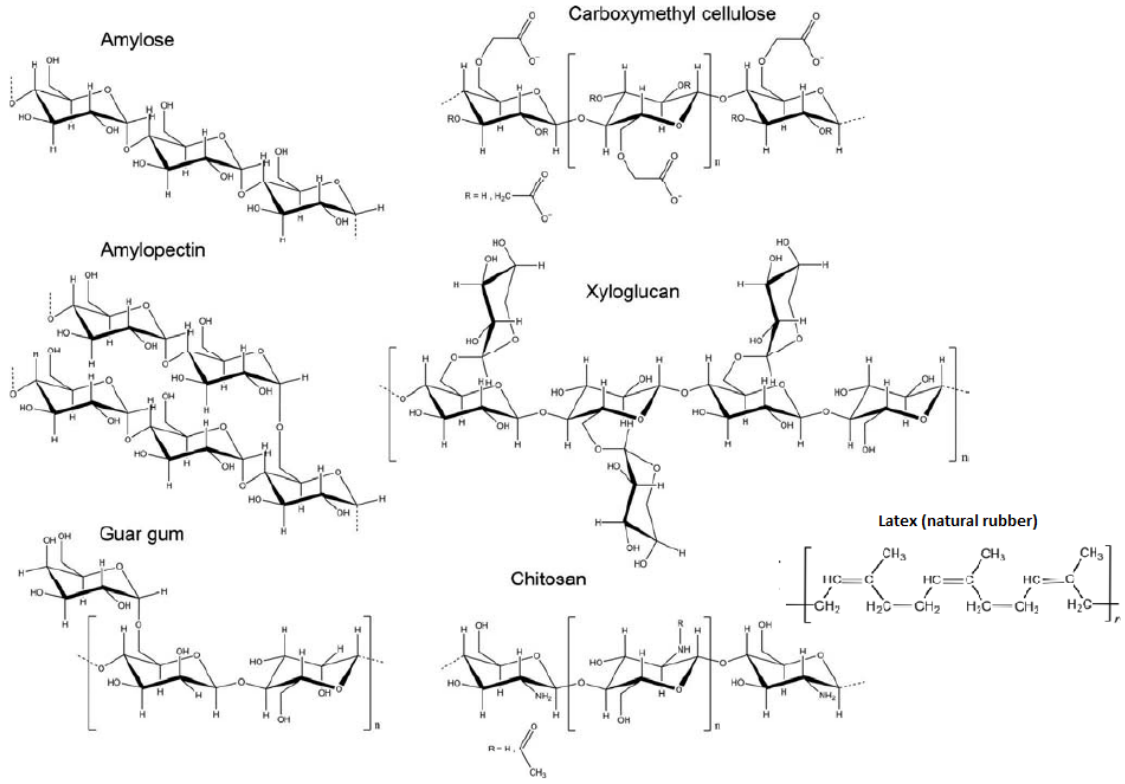


Figure 15. Conventional and non-conventional biopolymers used in papermaking. /adopted from 21/

Starch

The significant effects of the addition of starch on the strength and sizing of a paper were discovered in 3500-4000 B.C /44, p. 2/. Since those days the use of starch has continued and has increased steadily with increasing paper production. One reason for this is the abundance and the low price of the raw materials, combined with their high molecular weight and high hydrogen-bonding site density. The exact mechanism through which starch increases the strength of a paper is still unknown. Starch occurs in nature as small granules in the form of amylose and amylopectin. Depending on the plant, starch can contain up to 30% amylose and the rest is in the form of amylopectin /3/. Starch is a glucose polymer in which monomer units are linked to each other by a

1,4-α-D-glucosidic bond. Amylose is a linear chain polymer with a helical, semi-helical or open coil tertiary structure, whereas amylopectin consists of branches about 20-30 glucopyranose units long attached to the amylose backbone by α(1-6)-linked bonds /3; 41, p. 271/. The molecular weights of starches are challenging to measure and vary significantly from 10^3 to 10^7 g/mol, depending on the plant, separation/modification process and analytical method /3, 45, 46, p.606-607/. Native starch is fairly neutral in charge and has a small adsorption tendency on papermaking fibers because of the negative surface charge of the fibers. Therefore, the starch used in papermaking is usually cationized by quaternary ammonium groups. Starch is mostly used for the surface sizing but is also commonly utilized as a wet end additive /42, p. 69/. In the wet end, the dosage of cationic starch usually ranges between 0.2% and 2.5% of the wet end solids and the optimal degree of substitution usually varies between 0.015 and 0.04 and the charge density is then about 0.1-0.3 meqv./g. Starch stays cationic in the pH range 4-9. The optimal conductivity of white water for starch retention takes place below 2000 μS/cm when caused by monovalent ions. /3, 41, pp. 274-280/

Carboxymethyl cellulose

Carboxymethyl cellulose (CMC) is an anionic carboxyl group containing derivatives of cellulose. CMC is mostly used in coating a paper but can also be used as a wet end additive to improve the formation or water retention of fibers. The adsorption of anionic CMC on cellulosic fibers requires the use of a retention aid such as cationic polyelectrolytes or alum. Carboxymethyl cellulose is produced by reacting/etherifying hydroxyl groups of cellulose with chloroacetate /48/. The degree of carboxymethyl substitution (DS) of a cellulose molecule can vary from 1 to 3. The water solubility of carboxymethyl cellulose increases with increasing DS.

Lindström et al. (2005) reported that it could be possible to create higher strength in a paper sheet in comparison with cationic starch by 2% grafting of carboxymethyl cellulose (CMC) on bleached softwood kraft fibers by heating (80°C) and using suitable electrolytes. The effect of this kind of CMC grafting on the strength and breakage strain of a paper can be seen from Figure 16 /3/.

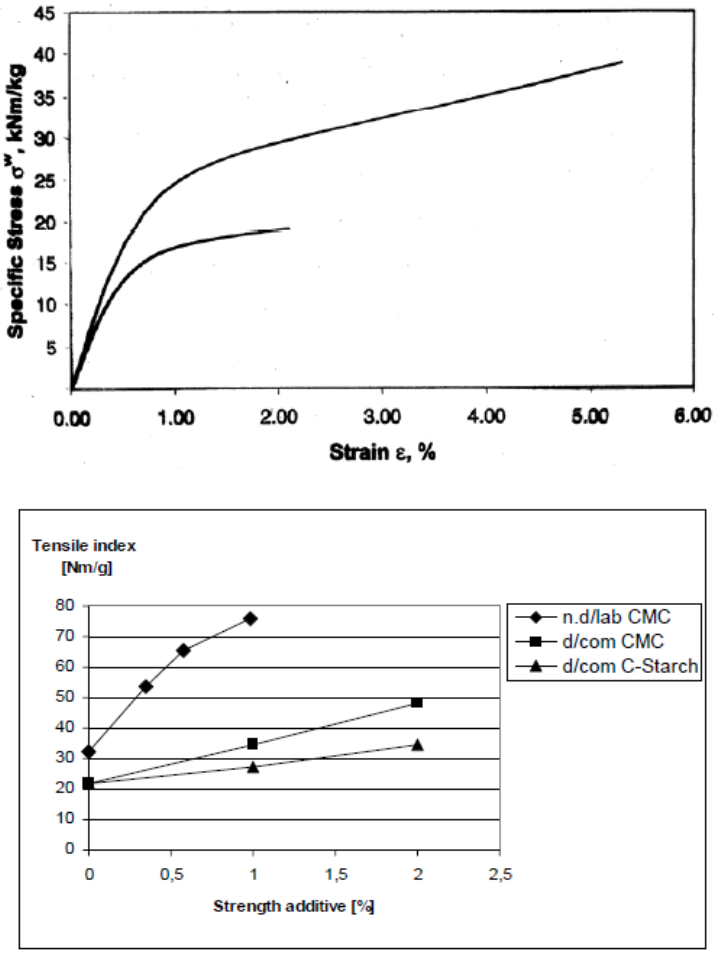


Figure 16. Load-elongation of BSK hand sheet with and without 2% CMC grafting (upper) and tensile index as a function of CMC and cationic starch dosage (lower). /3/

Chitosan

Chitosan is a linear carbohydrate polymer that consists of β(1-4) linked 2-amino-2 deoxy-D-glucose units. Chitosan is usually made from chitin by the hydrolysis of N-acetyl groups. Chitin is the second most abundant polysaccharide in the world and it is mostly found in the core structures of shellfish such as crab or shrimp. Chitosan has a high adsorption tendency on cellulosic fibers and it has been shown to be a 40% more effective binder than starch. High cost and uncertain availability limit the use of chitosan in papermaking.

Abdul et al. hypothesized in their work that a significant increase in the number of sites for hydrogen bonding results in a considerable improvement of inter-fiber bonding, which in turn increases the tensile strength. An increase of up to 57.8% in the tensile

index for kraft pulp sheet was achieved with the 1% addition of a soy flour-DTPA-chitosan additive, as can be seen from Table 5. /14/

Table 5. Mechanical properties of additive-treated OCC pulp hand sheets /14/.

dry strength additive	tensile index (Nm/g)	bursting index (KN/g)	STFI index (lbf/(g/m^2))
no additive	47.9	2.8	0.091
soy flour–DTPA–chitosan	73.1	3.9	0.128
soy flour–chitosan	52.8	3.4	0.109
soy protein flour–DTPA–chitosan	71.25	4.0	0.130
soy protein flour–chitosan	57.00	3.3	0.110
soy protein flour	49.28	2.7	0.093
acid hydrolyzed soy protein flour	48.5	2.8	0.091
soy flour (commercial)	50.29	2.9	0.096
native starch (commercial)	51.73	3.0	0.098
cationic starch (commercial)	55.1	3.1	0.102
cationic polyacrylamide (commercial)	56.0	3.2	0.107
anionic polyacrylamide (commercial)	50.7	2.9	0.092

[a]At 1.5% addition level, dried at room temperature, and cured at 105 °C.

Latex

Latex, i.e., natural rubber, is a polymer of isoprene monomers produced in a bark layer of rubber trees such as *Hevea brasiliensis*. Latex is sometimes used in the surface sizing or coating of a paper but rarely as a wet end additive. Latex is also a generic name for an emulsion of microscopic polymer particles. With the adsorption of 20% anionic polylactide latex as a wet end additive on bleached softwood kraft fibers using 0.4% cationic polyacrylamide as a retention aid, it is possible to prepare hand sheets with a nominal strain at breakage of 21%. This was achieved for cold-pressed, hot-pressed (150 °C) and non-dried hand sheets using hydroforming equipment with a double-curved mold /17/. The adsorption of 5% cationic latex as a wet end additive with certain styrene-butadiene proportions, it is possible to increase the tensile index of an unbeaten bleached kraft hand sheet from about 28 Nm/g to about 81 Nm/g. With 10% addition, the breaking length increased from about 4 km to about 7.8 km /38/.

Gums

Gum is a generic name for plant cell wall carbohydrates which are linear, heterogenic, slightly branched, polysaccharide-based hydrocolloids that form highly viscous gels or dispersions in a suitable solvent. Gums such as guar gum, locust bean gum and tamarind gum have the most commercial relevance in the food, textile and paper industries but in total there are about 30 natural and derivatized gums on the market /49, p. 91/. Guar gum is the gum most commonly used in papermaking to improve formation and dry strength. Gums in their native form do not have a surface charge but they have a natural affinity for cellulosic fibers. Gums are usually etherified with non-ionic, anionic or most commonly cationic components in order to increase the adsorption rate and extent on cellulose fiber surfaces. /23, pp. 67-92; 49, pp. 61-91/

Hemicelluloses

Hemicelluloses are very similar to gums by definition, with the difference being that they also contain glucose, xylose and some other sugar monomers which gums typically do not contain. The major classes of hemicelluloses are glucans, xylans and mannans. The quantity and quality of hemicelluloses varies significantly between and within plants, as can be seen from Table 2. Hemicelluloses such as glucuronoxylans have a negative surface charge because of the uronic acid groups, whereas xyloglucan and glucomannan have a neutral surface charge. Therefore, the affinity of negatively charged hemicelluloses for cellulosic fibers is poor. The use of hemicelluloses as papermaking additives is limited by their high separation costs, low molecular weight and poor charge properties, which are the reasons for their high price and low availability. Currently, hemicellulose does not have significant commercial importance as an additive in paper and board manufacturing.

Table 6. Occurrence of hemicelluloses in plants /50/.

Amount of polysaccharide in wall (% w/w)[a]						
	Dicot walls		Grass walls		Conifer walls	
Polysaccharide	Primary	Secondary	Primary	Secondary	Primary	Secondary
Xyloglucan	20–25	Minor	2–5	Minor	10	–[b]
Glucuronoxylan	–	20–30	–	–	–	–
Glucuronoarabinoxylan	5	–	20–40	40–50	2	5–15
(Gluco)mannan	3–5	2–5	2	0–5	–	–
Galactoglucomannan	–	0–3	–	–	+[b]	10–30
β-(1→3,1→4)-glucan	Absent	Absent	2–15	Minor	Absent	Absent

Nanofibrillated cellulose

Cellulose nanofibrils are nano-scale substructural units of cellulose fibers which have at least one dimension in the range of 1-100 nm. Their typical width is between 5 and 50 nm and their length is a few micrometers /54/. Cellulose nanofibrils can be isolated by mechanical disintegration after enzymatic hydrolysis or chemical pretreatment (TEMPO-oxidation) of the fibers. As a result of the pretreatment methods that have been developed there are commercial nanofibrillated cellulose products available on the market and their use is increasing in some applications. Nanofibrillated cellulose (NFC), as well as cellulose in general, typically has a negative surface charge as a result of carboxymethylate, carboxylate or sulfonate groups, depending on the chemical treatment. For papermaking applications NFC can be cationized by introducing quaternary ammonium groups or used together with a cationic retention polymer such as PAE or CPAM. Thin cellulose nanofibrils are flexible and have potential as an additive for the production of extensible films and paper with good barrier properties. /15, 54/

2.4.2 Synthetic polymers

Synthetic polymers are man-made polymeric substances containing different kinds of functional groups. The typical functionality of synthetic polymers used in papermaking is ionicity and polymers of this kind are called polyelectrolytes because they contain ionic or ionizable groups. In papermaking, synthetic polymers are often called resins and they are most commonly used for wet and dry strengthening. This section introduces the most commonly used and potentially useful synthetic polymers for increasing the strength and extensibility of a paper. Figure 17 shows the molecular structures of acrylamide- and polyamideamine epichlorohydrin-based polymers.

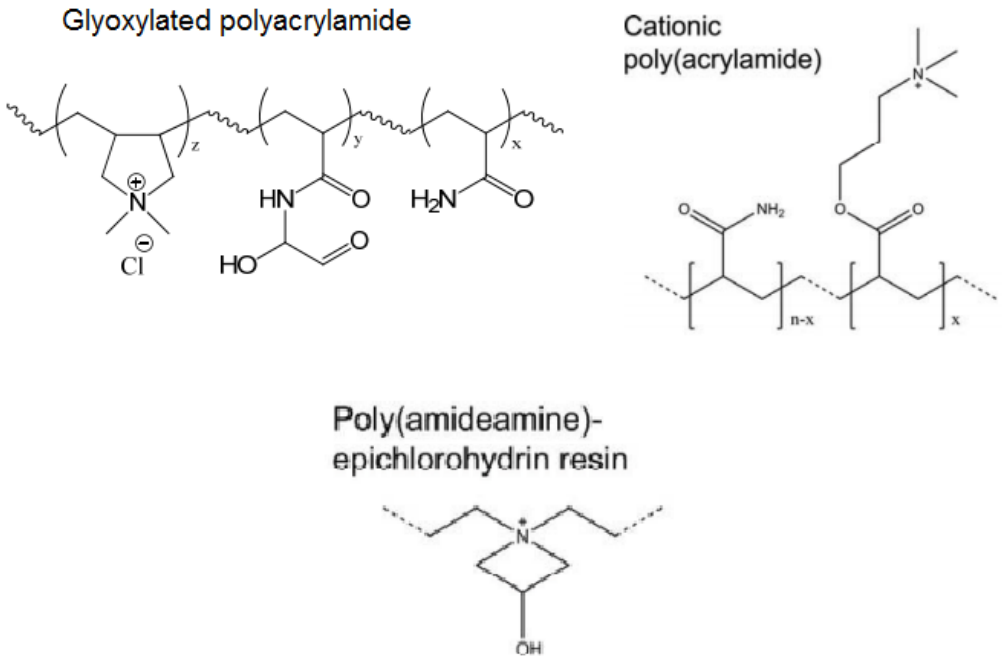


Figure 17. Typical synthetic polymers used in papermaking. /21,48/

Polyacrylamides

The first synthetic polymeric additive for papermaking, polyacrylamide, was developed in the middle of the 20th century. Thanks to its water solubility and high hydrogen bonding capacity, it has turned out to be excellent for the dry strengthening of a paper. The reason for its development was the development of acrylamide monomer from acrylonitrile and, of course, the cheap raw material, oil /23, pp. 125-148/. In the case of amphoteric polyacrylamide both cationic and anionic groups are present. The molecular weight and charge density can vary greatly but are typically in the range of 100-2000 kDa and 1-10 mol-%, respectively /48/. Amide groups increase the number of hydrogen bonding sites, which makes a significant contribution to the dry strength of the paper. /52, pp. 1-62/

Polyamineamide epichlorohydrin

The lack of wet strength of paper led to the development of formaldehyde-based polymers during and after the Second World War. Environmental regulations and the need for neutral and alkaline papermaking polymers led to the development of polyamineamide epichlorohydrin (PAE) and other wet-strength resins. Polyamineamide epichlorohydrin is sometimes called polyaminoamide epichlorohydrin or polyamide epichlorohydrin. PAE polymer consists of a polyamineamide backbone which is reacted

with epichlorohydrin to produce azetidinium ion groups, which, in turn, provide self-cross-linking and cationic charge functions. The wet strengthening mechanism is based on cross-linked PAE, which forms a waterproof surface around the inter-fiber bond and prevents water from hydrolyzing it. PAE also contributes to the dry strength, which, in turn, probably contributes to some extent to the extensibility of a paper. /53, pp. 1-36/.

Glyoxalated polyacrylamides

Glyoxylated polyacrylamide (GPAM) and PAE are the two most commonly used wet-strength resins in paper and board manufacturing. Unlike PAE, GPAM can form covalent bonds in the inter-fiber contact area when paper is in a dry state. The amide group and covalent bonding ability of glyoxal increase the dry strength of a paper containing GPAM more than other traditional additives do. The covalent bonding ability with cellulose is reversible in water, which gives the paper temporary wet strength. GPAM is manufactured by cross-linking cationic polyacrylamide with glyoxal. /53, pp. 45-61/

2.4.3 Other chemical additives

The wet strengthening of a paperboard is mostly based on covalent bonding at the fiber-polymeric additive-fiber interfaces, i.e., inter-fiber bonds, whereas dry strengthening is mostly based on hydrogen bonding. In order to increase the extensibility of a dry paperboard, sufficient breakage and reformation, i.e., the rearrangement of hydrogen bonds, are needed without the breakage of the paperboard sheet. Chemicals that interfere sufficiently with the hydrogen bonding of cellulose fibers in this way are called plasticizers. To some extent most of the biopolymers and synthetic polymers described earlier act as plasticizers, although their primary function is to increase the number of hydrogen and/or covalent bonds. One plasticizer which can be used together with polymeric additives is glycerol.

McQueen, Mason and Cosgrove studied the effect of the addition of plant cell wall proteins, cellulase enzyme and urea on the extensibility of pure cellulose filter paper. They discovered that treatment with an 8-M urea solution caused very rapid extension and breakage of the paper, whereas protein with a concentration of 5 µg/l caused significant and equal extension and strain at breakage in a similar way to cellulase with a concentration of 100 ug/l. 2 M urea treatment doubled the expansion rate of both

protein-treated and non-treated paper but without protein and using only 2 M urea, the extension was very slow. /13/

2.5 Summary of the literature review

The aim of this literature review was to provide relevant background information, justify the choice of polymers, investigate the test methods and clarify the importance of the topic. The extensibility of paperboard is governed by the properties of the fibers, the fiber network, inter-fiber bonding and external factors. Starch is the most common paperboard strength additive and is known to increase the extensibility of paperboard by a few percent. Starch is a cheap additive but forms relatively brittle paperboard. Therefore it is not suitable for high-extensibility paperboard grades. In the case of starch-added paperboards, by applying optimized properties of fibers, the fiber network and external conditions via beating, drying shrinkage, temperature and moisture, an increase of ca. 10% in extensibility is achievable. However, within the ACel project the target extensibility of thermoformable packaging material is 30%. Generally, several phenomena in papermaking are strongly related to the chemistry at the solid surfaces and interfaces. The surface chemistry of the fibers affects the properties of the fibers and inter-fiber bonds and they in turn affect the fiber network properties in terms of retention, dispersion, aggregation and formation. Hence, it is obvious that the modification of the fibers and inter-fiber bonds using chemical additives is a reasonable way to increase the extensibility of paperboard towards the target 30%.

When a paperboard is subjected to a load it starts to deform until the point of rupture. The rupture is initiated by a sufficient number of breakages of fibers, fibrils and/or inter-fiber bonds at the weakest spot in the network. Because the rupture of a paperboard is mainly due to the breakage of the inter-fiber bonds and because all the mechanical properties of a paperboard, such as extensibility, exist because of the inter-fiber bonds, it can be assumed that the inter-fiber bonds and their number and type are the main parameters in the creation of additional extensibility. Here it can be assumed that the chemicals that have potential are the ones that increase both the strength and plasticity of the inter-fiber bonds, leading to higher tensile strength and a higher breakage strain of the paperboard. The individual strength of an inter-fiber bond can be improved by increasing the number and/or type of molecular bonds. However, the

plastic deformation of inter-fiber bonds as a molecular-level phenomenon is not very well understood. It is likely that temporarily reducing the number, or deactivating a part of the hydrogen bonds via increased moisture content, higher temperature and/or improving their rearrangement capacity or ability to slip and rebond, increases the plasticity of the matrix. Enhancing the inter-fiber bond area – the relative bonded area – of a paperboard is another way to increase both the tensile strength and breakage strain of a paperboard. To some extent this can be done, for example, by increasing the fiber swelling, i.e., their compliance, and a higher wet pressing pressure in order to reach the targeted 30% extensibility level. However, high dosages of chemical additives are probably needed for such an approach. Typically, the paperboard additives that contribute to tensile strength and breakage strain are polymeric substances. Because of the negative net surface charge of cellulosic fibers, polymeric additives need to carry some cationic groups/charges in order to chemisorb effectively onto fibers. The molecular weight, charge density and structure of a polymeric additive are generally known to contribute significantly to the mechanical properties of paperboard.

3. Experimental part

3.1 Materials

The methods and materials used in this thesis are described in this chapter.

3.1.1 Pulp

The fiber raw material used in this work was ECF-bleached, once-dried Kaukopää softwood kraft pulp with the following characteristics: viscosity 810 ml/g (ISO 5351), Mn = 797600 g/mol (SEC-RI, LiCl/DMAc), Mw = 53900 g/mol (SEC-RI, system, pullulan), SR° = 12 (ISO 5267/1), WRV = 1.08 g/g (SCAN-C 62:00). The chemical composition was lignin 0.9%, cellulose 83.3%, xylan 10.4% and glukomannan 8.4% (NREL/TP-510-42618). The metal content of the pulp was, on an mg/kg basis, Ca 240, Cu <0.5, Fe 190, Mg 170, Mn <0.3, Na 250 and Si 37.

3.1.2 Polymers

Table 6 shows 17 different polymers or polymer combinations which were tested with dosages of 5, 10, 20 and 50 kg/dry ton of pulp. The polymer combinations were selected on the basis of the performance of the individual polymers. The viscosities of the

polymers were measured from water solutions at 25 °C according to Kemira's instructions /103/. The viscosities, especially of the CMC and CPAM polymers, were measured to get some kind of correlative parameter from the molecular weights.

Table 7. The polymers investigated in this study.

Polymer	Product description
Cationic starch	Nitrogen: 0.27-0.31%, V1.0% 173 mPas, 18/12
Chitosan HMW	Viscosity of 1% solution in 1% acetic acid 3070 mPas
Chitosan LMW	Viscosity of % solution in 1% acetic acid 47 mPas
CMC LMW	V0.5%: 10 mPas, 18/60
CMC HMW	V0.5%: 404 mPas, 18/6
Cationic guar gum	Cationized guar gum, V0.5% 230 mPas, 18/12
Cationic NFC	Charge at pH 4 and 7 is 1.4 meq/g (DS 0,3). Preparation at 2% consistency under 1000 bar with 2 circulations. V1.0%: 216 mPas, 18/12.
PLA latex	pH: 4.2, DS: 40.2%, viscosity: 750 mPas
PAAE high ECH	Polyamidoamine resin, high epichlorohydrin treated. V: 27 mPas, 18/60
PAAE low ECH	Polyamidoamine resin, low epichlorohydrin treated. V: 90 mPas, 18/30
GPAM	Glyoxylated cationic polyacrylamide, V10% 35 mPas, 18/60
CPAM 1	10 mol-% cationic polyacrylamide, V0.5% 10 mPas, 18/60
CPAM 2	10 mol-% cationic polyacrylamide, V0.5% 72 mPas, 18/30
CPAM 3	6 mol-% cationic polyacrylamide, V0.5% 193 mPas, 18/12
CPAM 4	2 mol-% cationic polyacrylamide, V0.5% 39 mPas, 18/60
PAH	Cationic polyallylamine, Mw ~58000 g/mol, V10% 6.5 mPas, 18/60
HA	Anionic glucosaminoglycan, sodium salt form, V0.5% 307 mPas, 18/6

3.3 Methods

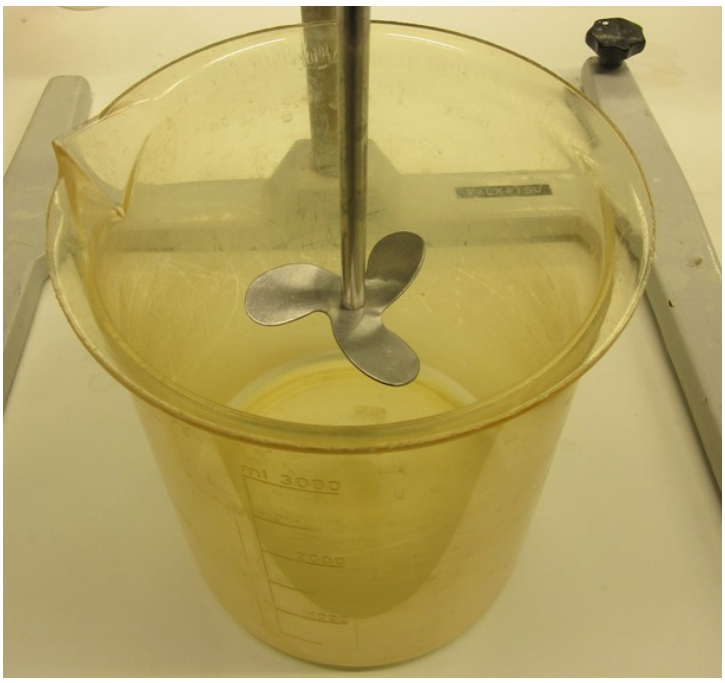
3.3.1 Dry matter content and beating

The dry matter content of the air dry pulp was determined according to ISO 638 with the following exceptions /101, p. 97/. A 10-min rapid drying in a grill was used instead of overnight oven drying at 105 °C. Separate wet disintegration was not needed because

the fibers became disintegrated during beating according to the standard ISO 5264/1, which utilizes a Valley beater /101, p. 627/. A suitable beating time was 47-51 minutes, which enabled a reasonable dewatering time in a sheet former with high polymer dosages of all the polymers except cationic guar gum, which required a few minutes' dewatering time and double-side prepressing. The degree of beating was determined by the SR (Shopper-Riegler) number, which was SR°25-28 after a beating time of 47-51 min. A batch of beaten pulp suspension was used for one week.

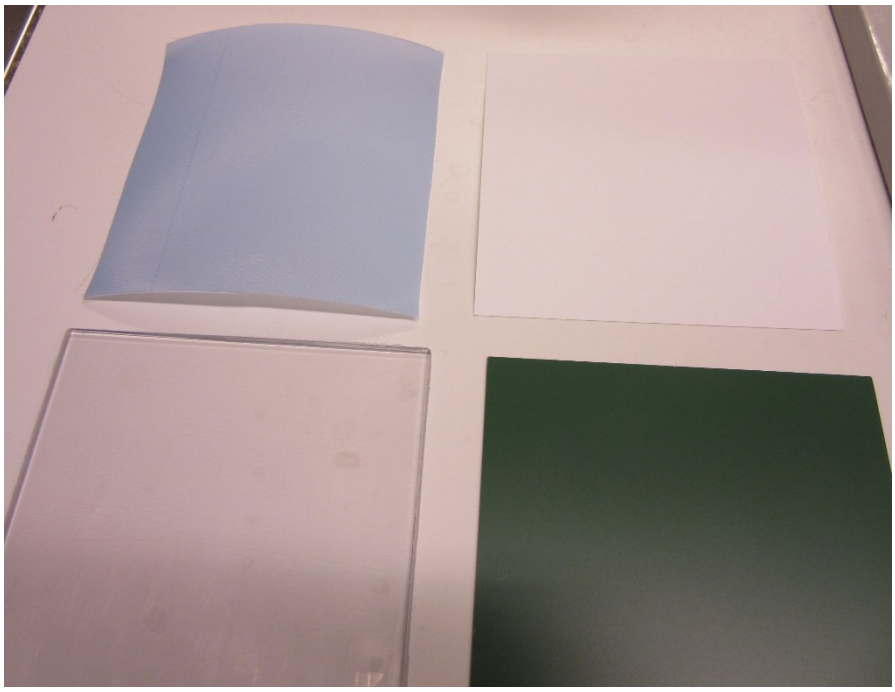
3.3.2 Stock and paperboard hand sheet preparation

The stock and hand sheets were prepared from beaten pulp according to the ISO 5269/1 standard, with the following exceptions /101, p. 683/. Tap water was used for the pulp beating and stock dilution. Five mmol/l of NaCl was added to the 0.4% stock at least five minutes prior to the addition of the polymer. Reference sheets (without the addition of polymer) were prepared from every beaten pulp batch. The polymer was added as a 0.2% (dry polymers) or 1% (solution polymers) solution to a separate stock sample sufficient for preparing one hand sheet. After the addition of the polymer the stock was mixed in a three-liter beaker for 90 seconds with a speed mixer (2000 rpm) using a three-blade propeller, as shown in Picture 1.



Picture 1. Container and mixing propeller (3*~3cm) used for mixing the polymer into the stock.

In the case of using two different polymers, i.e., bi-layering, the second polymer was added immediately after 90 sec of mixing at 2000 rpm and the mixing was repeated. After the mixing, the stock was poured into the hand sheet forming vessel and diluted to about 9.7 liters (0.03% consistency), which was determined to give a reasonable formation and dewatering time, including with high polymer dosages. A lower furnish volume of 4.0 liters (0.08% consistency) was also tested with higher polymer dosages. The dewatering time was measured from the first three sheets with an accuracy of one second. The wet pressing of the sheets had to be carried out between a polycarbonate drying plate and the forming wire to avoid the sheets becoming glued to the suction board with high polymer dosages. After wet pressing the sheets were dried and conditioned overnight at 50% RH/23 °C under strain so that the screen wire was removed and the sheet was between a cloth and a smooth polycarbonate drying plate. The different drying plates are shown in Picture 2.



Picture 2. Drying plates: polycarbonate (transparent), traditional (green), screen wire (blue) and suction board (white).

3.3.3 Determination of the tensile strength and strain at breakage

The tensile strength and strain at breakage were determined according to the ISO 1924-3 standard using an L&W horizontal tensile tester as shown in Picture 3 /102/. A tensile

test was also carried out for strips of paperboard conditioned at 80% RH / 23 °C for at least four hours. The tensile strength and strain at breakage results were normalized with respect to the reference sheet.

Picture 3. Horizontal tensile tester.

3.3.4 Determination of grammage and thickness

The grammage of the hand sheets was determined according to the ISO 536 standard /101, p. 83/. The thickness was determined according to the ISO 534 standard /101, p. 67/.

3.3.5 Formation determination

The formation of the hand sheets was checked by visual observation immediately after their formation. Photographs were taken in case something unusual appeared in the dried sheets and beta-formation analysis was carried out to get numeric formation values.

4. Results and discussion

The results and discussion part is divided into three parts. In the first part the effects of natural polymers are reported and discussed. The second part deals with the effect of synthetic polymers on the paper properties. The third part concentrates on the effect of using two polymers, i.e., bi-layering of fibers, on the paper properties. The last part

summarizes the results and discusses them with respect to the literature review. It was noticed in the pre-tests with higher polymer dosages (over 100 kg/t of dry pulp) that standard methods for the preparation of the paper hand sheet were not completely applicable. This was because some of the polymers increased the dewatering time by hundreds of percent and made the hand sheets too sticky to be detached from the suction board and drying plate after wet-pressing. Hence, the highest polymer dosage was selected to be 50 kg/t and polycarbonate drying plate material was used instead of the traditional drying plate. The traditional suction board was also replaced with a forming screen in the wet-pressing. However, there were differences between the polymers and dosages in terms of the force needed to detach the paper sheets from the polycarbonate drying plate by hand after drying. For example, with the polymer combination GPAM + HMW CMC (50% + 50%) paper sheets detached from the polycarbonate drying plate by themselves during the drying and became wavy (see Other effects). Therefore, the rest of the tests (tests 88-110) and those with the greatest potential that had already been performed were carried out using traditional drying plate material and a suction board (see Additional tests). The measurement data of all the tests can be found in Appendix 1.

4.1 Effect of natural polymers on paper properties

LMW chitosan could be dissolved in 0.12% adipic acid but not HMW chitosan. Therefore, both chitosans were dissolved in 0.24% adipic acid. Chitosan HMW did not dissolve in 0.24% citric acid in two hours. For this purpose 0.5, 1.0, 2.0, 4.0 and 8.0% citric acid concentrations were tested to screen the required amount. After overnight mixing, the 0.5% and 1.0% citric acid solutions contained significant amounts of undissolved chitosan but the 2.0%, 4.0% and 8.0% citric acid solutions looked similar, although a few undissolved chitosan flakes occurred. On the basis of this a 2.0% citric acid concentration was selected for the dissolution of HMW chitosan.

4.1.1 Breakage strain

None of the polymers with 5 to 50 kg/t oven dry pulp dosages increased the breakage strain significantly at either relative humidity, which can be seen from Figures 18-21. However, tests performed with a smaller 4.0-liter furnace volume (9.7 liters in the other tests), i.e., at a higher forming consistency (0.08%) using cationic starch indicated that

using a higher furnish consistency it could be possible to improve the breakage strain significantly, as can be seen from **Error! Reference source not found.** and 20. Stress-strain data were not available from the tensile test, except the maximum force and elastic modulus. Therefore, the parameters given in Table 2, for example the true plastic strain, could not be calculated. The true plastic strain might have given useful information since it is the plasticity that contributes more to the extensibility after a about 3% in tensile strain.

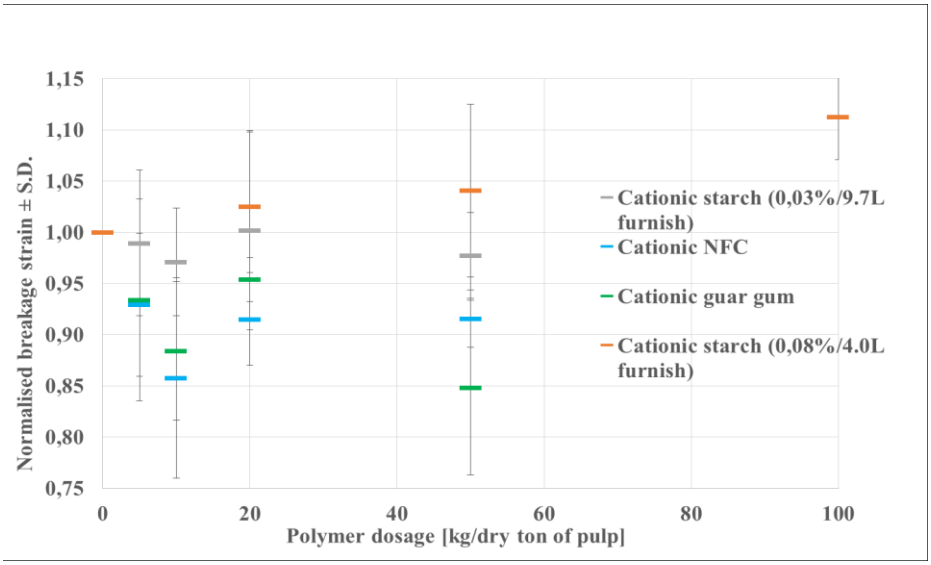


Figure 18. Effect of cationized natural polymers on in-plane breakage strain of paper hand sheet at 50% RH. (Abs. breakage strain of ref. sheets: Cat starch (0.03%/9.7L) = 4.0%, Cat NFC = 4.2%, Cat guar gum = 4.2% and Cat starch (0.08%/4.0L) =3.6%.

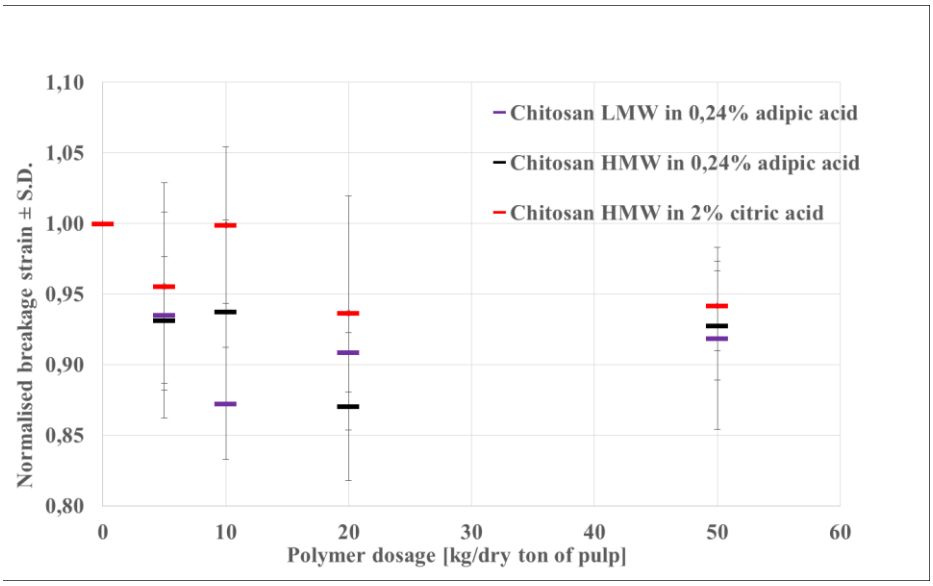


Figure 19. Effect of chitosan on in-plane breakage strain of paper hand sheet at 50% RH. (Abs. breakage strain of ref. sheets: LMW/adipic acid = 4.0%, HMW/adipic acid = 4.1% and HMW/citric acid = 4.1%)

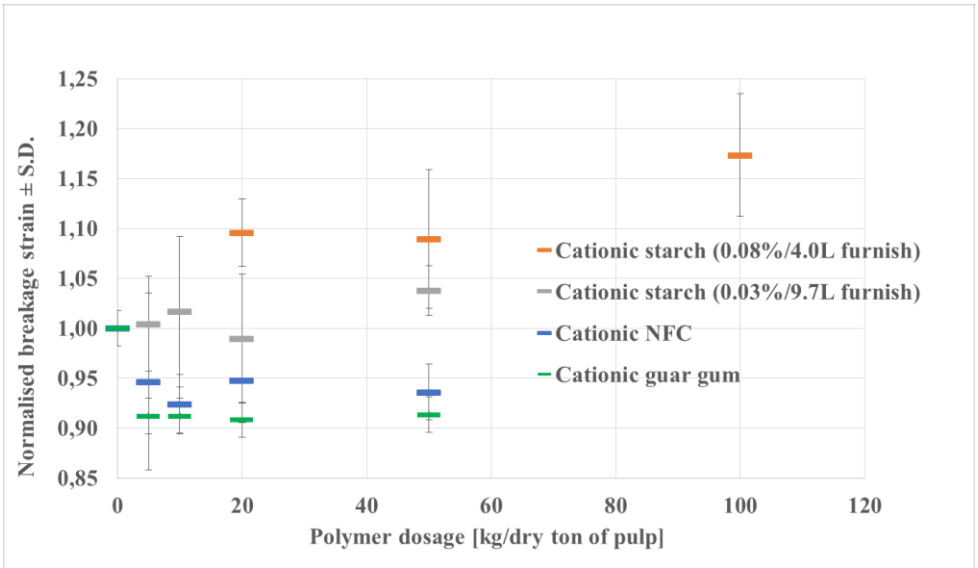


Figure 19. Effect of cationized natural polymers on in-plane breakage strain of paper hand sheet at 80% RH. (Abs. breakage strain of ref. sheets: Cat starch (0.03%/9.7L) = 4.3%, Cat NFC = 4.5%, Cat guar gum = 4.7% and Cat starch (0.08%/4.0L) = 4.0

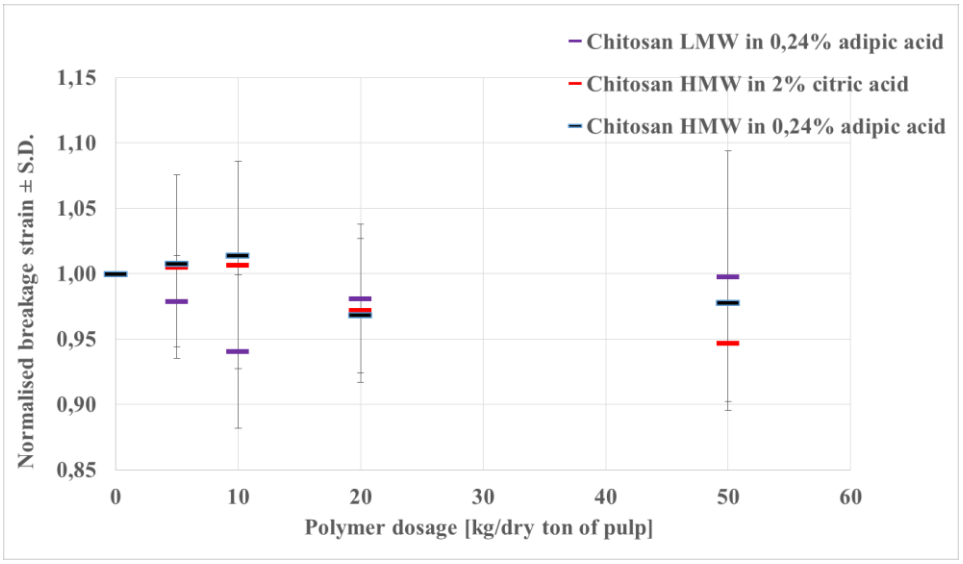


Figure 21. Effect of chitosan on in-plane breakage strain of paper hand sheet at 80% RH. (Abs. breakage strain of ref. sheets: LMW/adipic acid = 4.5%, HMW/adipic acid = 4.4% and HMW/citric acid = 4.4%)

4.1.2 Tensile strength

Cationic starch and cationic NFC significantly improved the tensile index of the paper sheet at 50% RH with the highest dosage, as can be seen from Figure 22. Cationic starch was significantly better than any of the other polymers and there were no differences between the other polymers, including chitosans, with any dosage at either relative humidity, as Figures 23-25 illustrate.

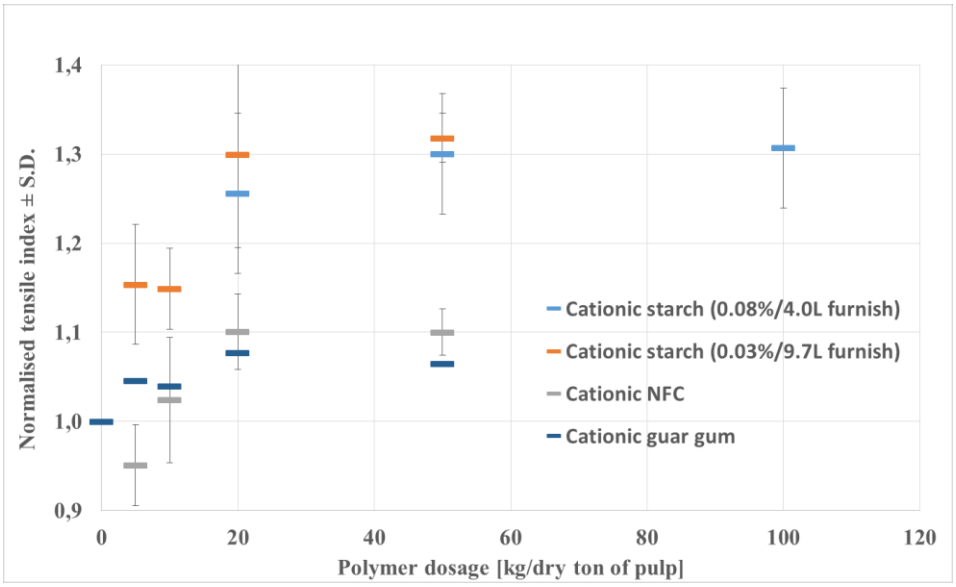


Figure 22. Effect of cationized natural polymers on tensile index of paper hand sheet at 50% RH. (Abs. tensile index of ref. sheets: Cat starch (0.03%/9.7L) = 67.7 Nm/g, Cat NFC = 74.2 Nm/g, Cat guar gum = 72.1 Nm/g and Cat starch (0.08%/4.0L) = 65.6 Nm/g)

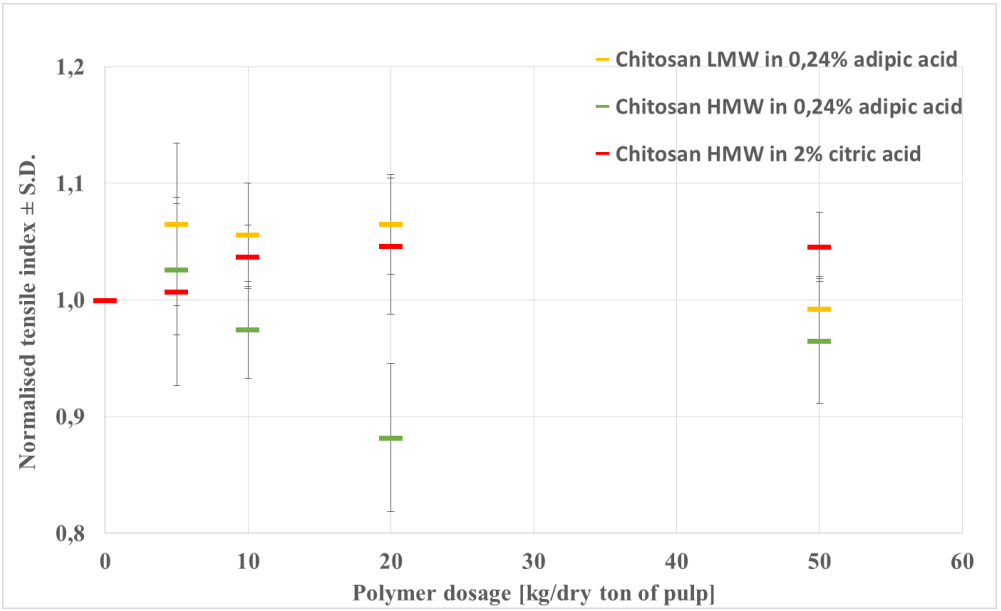


Figure 23. Effect of chitosan on tensile index of paper hand sheet at 50% RH. (Abs. tensile index of ref. sheets: LMW/adipic acid = 68.0 Nm/g, HMW/adipic acid = 70.5 Nm/g and HMW/citric acid = 70.5 Nm/g)

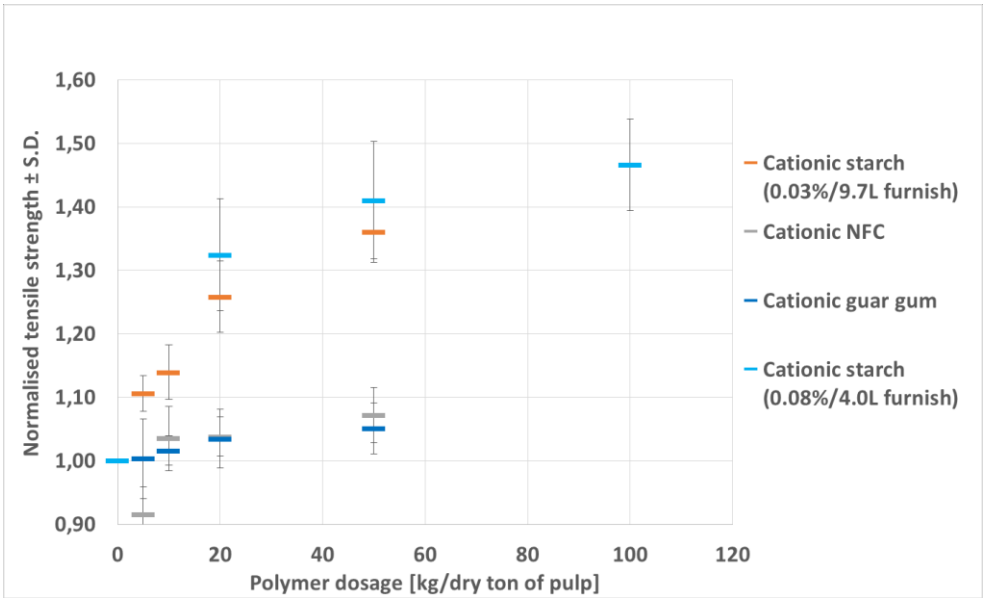


Figure 24. Effect of cationized natural polymers on tensile strength of paper hand sheet at 80% RH. (Abs. tensile strength of ref. sheets: Cat starch (0.03%/9.7L) = 7.3 kN/m, Cat NFC = 7.7 kN/m, Cat guar gum = 7.8 kN/m and Cat starch (0.08%/4.0L) = 6.3 kN/m)

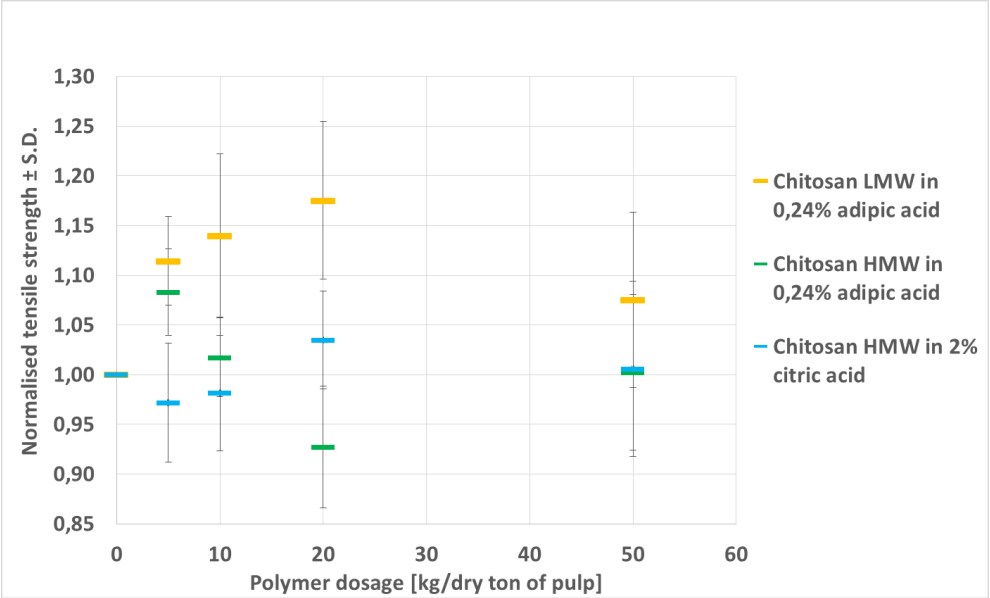


Figure 25. Effect of chitosan on tensile strength of paper hand sheet at 80% RH. (Abs. tensile strength of ref. sheets: LMW/adipic acid = 7.3 kN/m, HMW/adipic acid = 7.4 kN/m and HMW/citric acid = 7.4 kN/m)

4.1.3 Hand sheet formation

Unexpectedly, cationic starch (0.03%/9.7L), cationic guar gum and cationic NFC improved the beta-formation significantly as the dosage increased, which can be seen from Figures 26 and 27. Chitosan HMW in 2% citric acid improved the beta-formation significantly, with the highest dosage reaching almost the same level as the three

mentioned earlier. Chitosan LMW in 0.24% adipic acid was significantly better than chitosan HMW in 0.24% adipic acid with medium dosages. There were no significant differences between chitosan LMW in 0.24% adipic acid and chitosan HMW in 2% citric acid, although the latter showed a decreasing trend and the former showed an increasing trend in the beta-formation number.

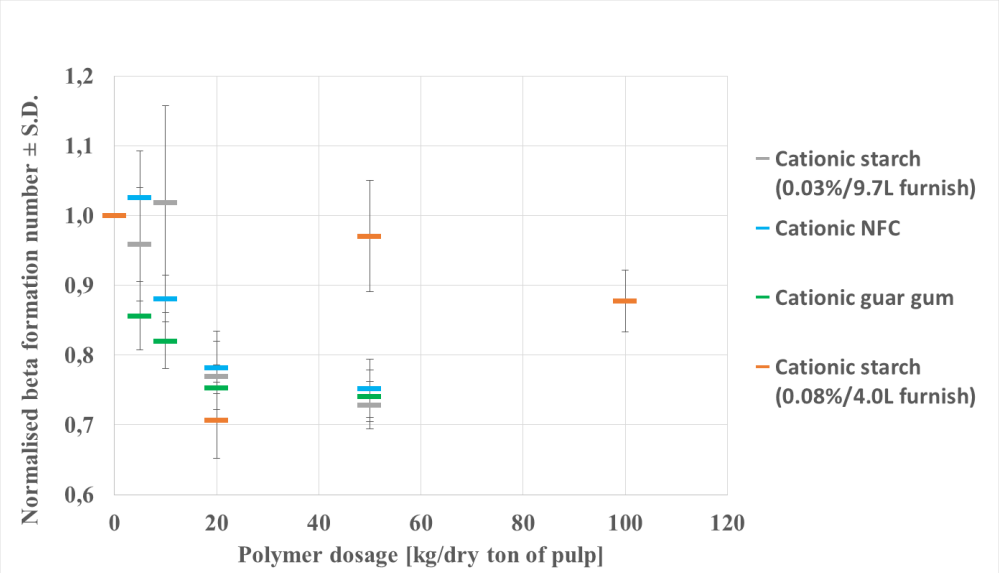


Figure 26. Effect of cationized natural polymer on beta-formation of paper hand sheet at 50% RH. (Abs. beta-formation of ref. sheets: Cat starch (0.03%/9.7L) = 6.8, Cat NFC = 6.0, Cat guar gum = 6.1 and Cat starch (0.08%/4.0L) = 7.7)

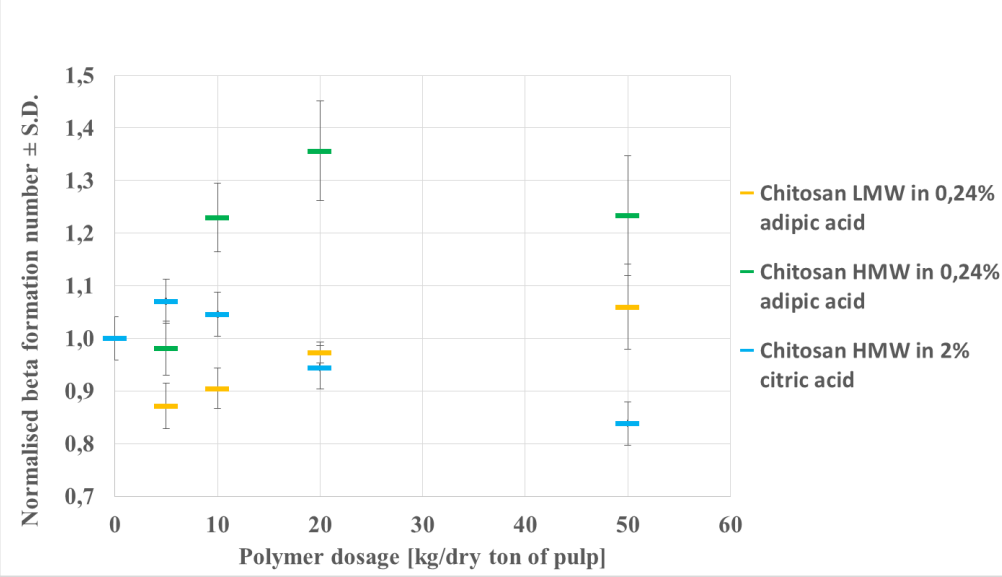


Figure 27. Effect of chitosan on beta-formation of paper hand sheet at 50% RH. (Abs. beta-formation of ref. sheets: LMW/adipic acid = 6.8, HMW/adipic acid = 6.3 and HMW/citric acid = 6.3)

4.1.3 Other effects

The dewatering time was 9 to 12 seconds with all the polymers and dosages except with the highest dosage of cationic starch and cationic guar gum, which increased the dewatering time up to 14 to 15 seconds, as can be seen from Figures 28 and 29.

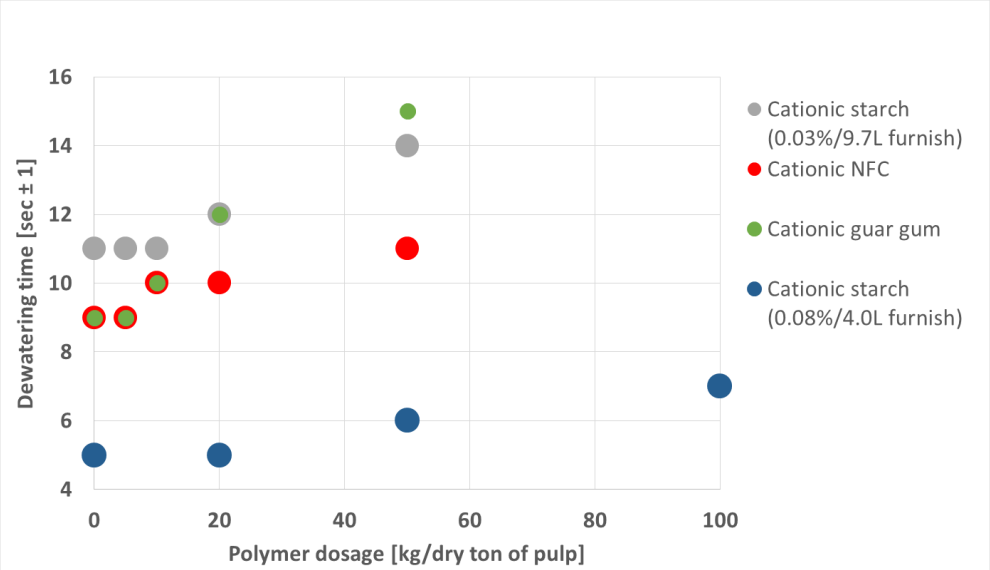


Figure 28. Effect of cationized natural polymer on dewatering time in paper hand sheet formation.

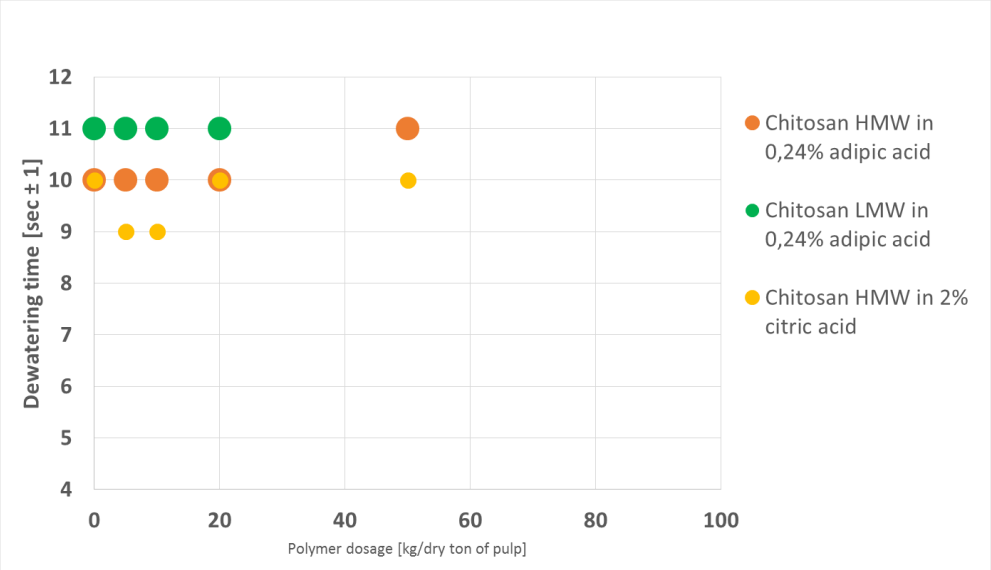


Figure 29. Effect of chitosan on dewatering time in paper hand sheet formation.

Figure 30 shows how the elastic modulus increases significantly with cationic starch, cationic guar gum and cationic NFC, while chitosan – Figure 31 – does not have a significant effect, except chitosan LMW in 0.24% adipic acid with the three lowest

dosages. Chitosan HMW with the two highest dosages appears to increase the elastic modulus in 2% citric acid more than in 0.24% adipic acid. Cationic starch with a lower furnish volume, i.e., a higher pulp consistency in sheet formation, shows a significantly lower modulus of elasticity than other cationized natural polymers with a 50 kg/t dosage.

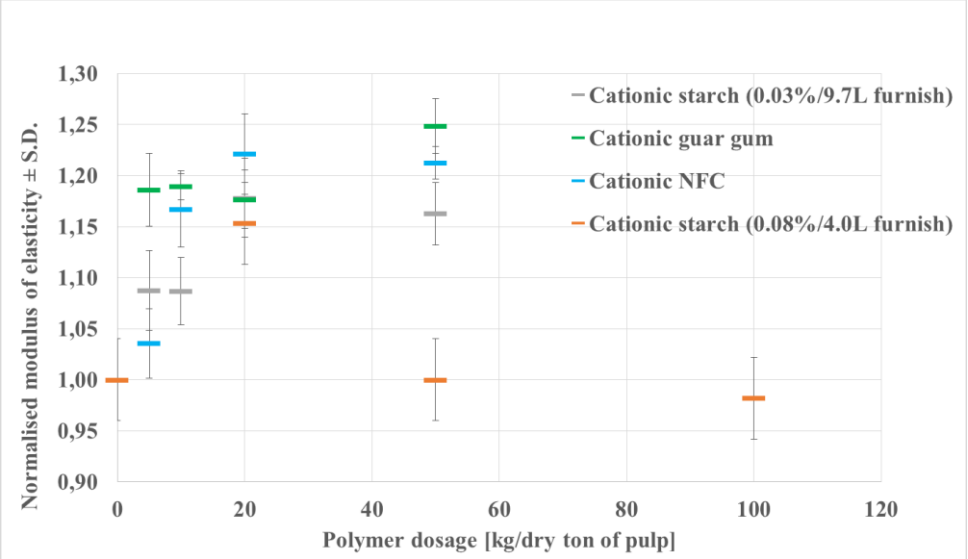


Figure 20. Effect of cationized natural polymers on modulus of elasticity of paper hand sheet 50% RH. (Abs. modulus of elasticity of ref. sheets: Cat starch (0.03%/9.7L) = 4.4 GPa, Cat NFC = 4.4 GPa, Cat guar gum = 4.2 GPa and Cat starch (0.08%/4.0L) = 4.5 GPa)

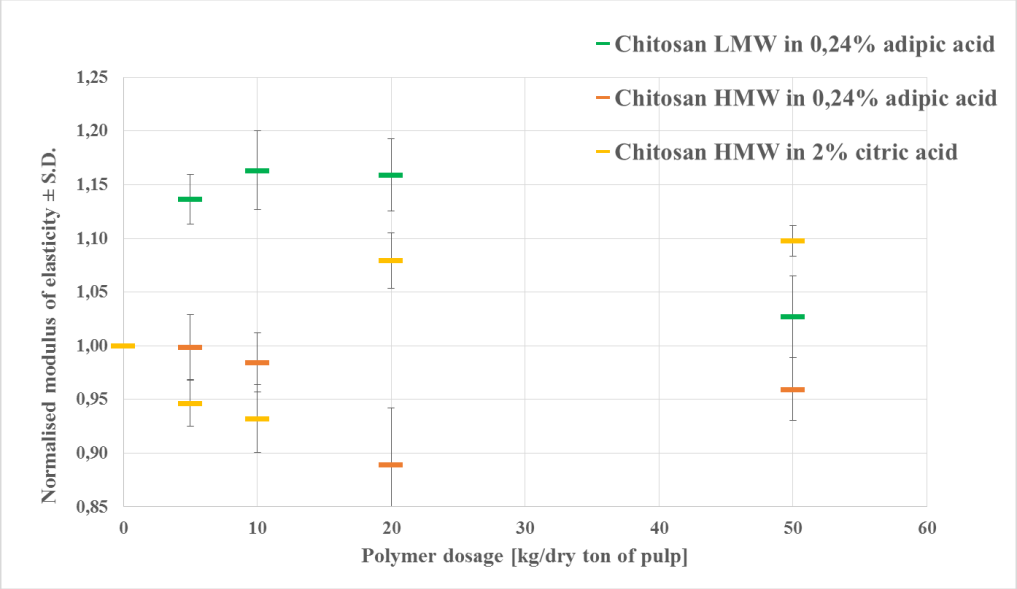


Figure 31. Effect of chitosan on modulus of elasticity of paper hand sheet at 50% RH. (Abs. beta-formation of ref. sheets: LMW/adipic acid = 4.2 GPa, HMW/adipic acid = 4.7 GPa and HMW/citric acid = 4.7 GPa)

Considering all the natural polymers that were tested, there is a relatively good correlation between the modulus of elasticity and density at 50% RH, as Figure 32 illustrates. This was an expected result, as would have been a generally decreasing breakage strain with an increasing modulus of elasticity, but it was not observed from the results, as can be seen from Figure 33.

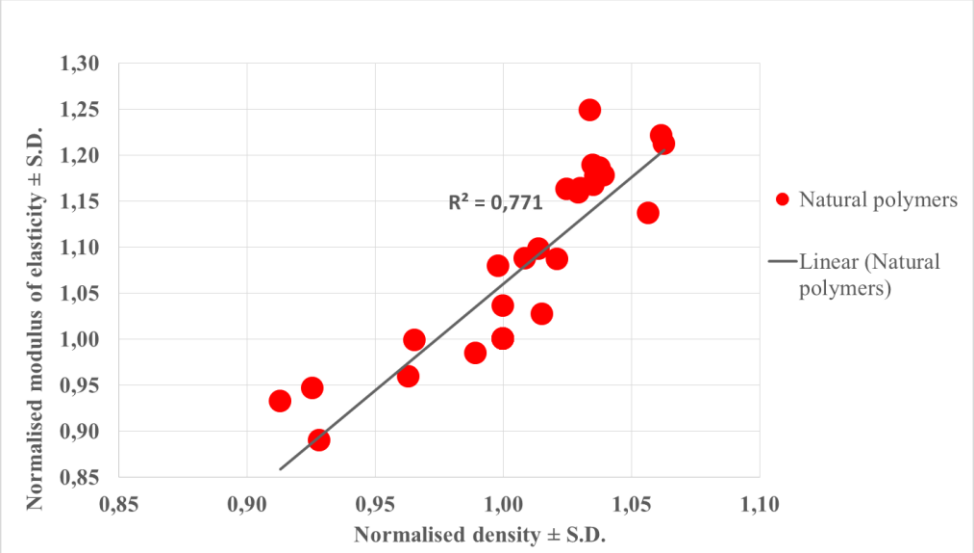


Figure 32. Effect of natural polymers on modulus of elasticity and density of paper hand sheet.

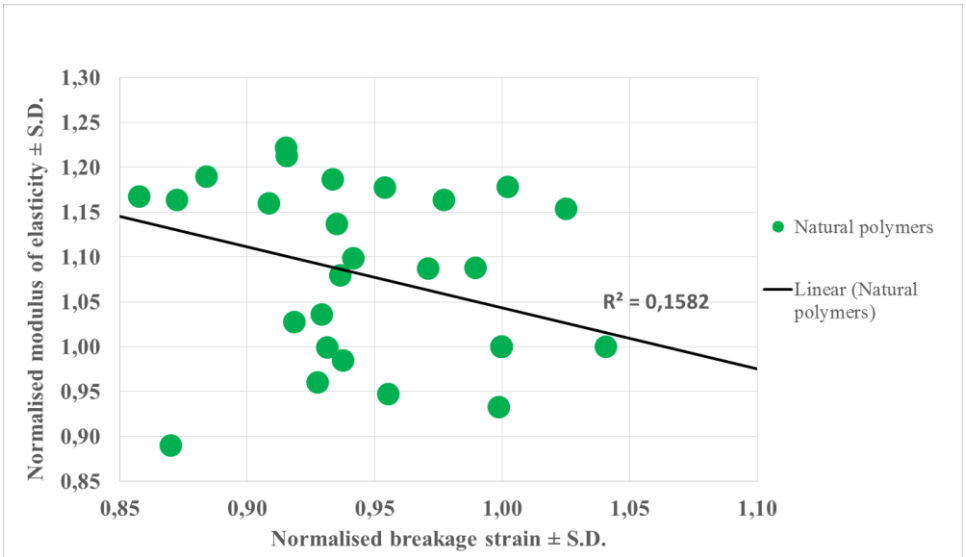


Figure 33. Effect of natural polymers on modulus of elasticity and breakage strain of paper hand sheet.

There was no correlation or a very low one between the breakage strain and tensile strength at both relative humidities among all the natural polymers, as can be seen from Figures 34 and 35.

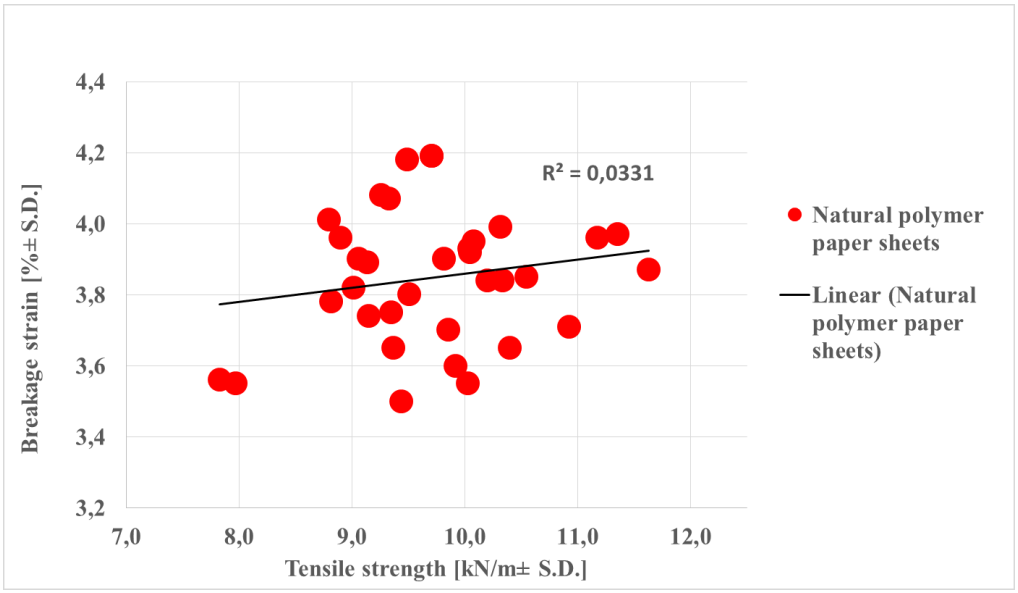


Figure 34. Effect of natural polymers on breakage strain and tensile strength at 50% RH.

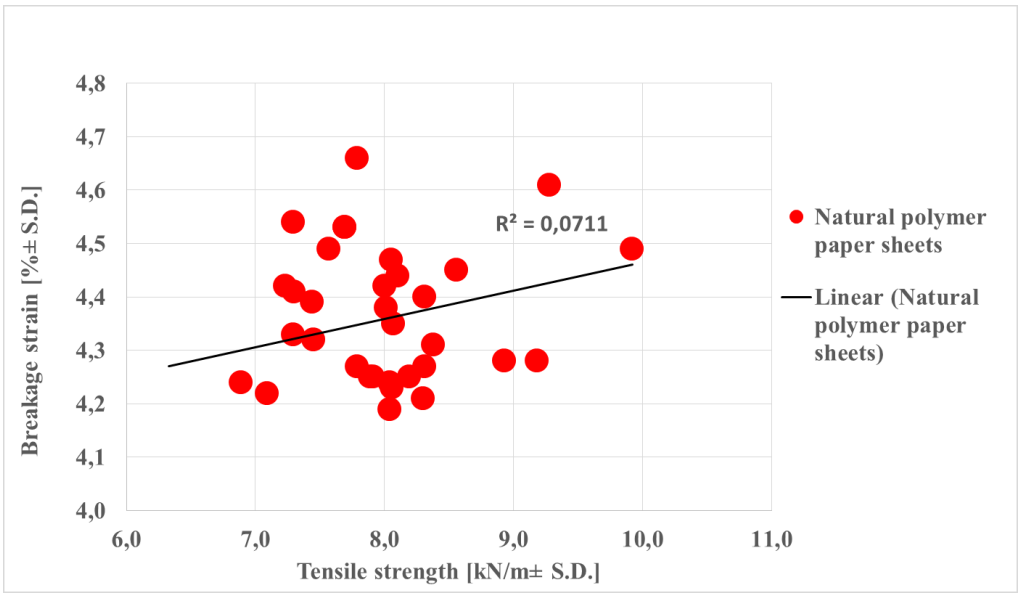


Figure 35. Effect of natural polymers on breakage strain and tensile strength at 80% RH.

4.2 Effect of synthetic polymers on paper properties

4.2.1 Breakage strain

GPAM was the only polymer that significantly increased the breakage strain with a 10 kg/t dosage at both relative humidities, as can be seen from Figures 36 and 38. Figures 37 and 39 show how CPAM 3 significantly reduced the breakage strain with the highest

dosage at both relative humidities. There were no significant differences between any polymers at either relative humidity, except between GPAM and CPAM 3, with the highest dosage at 50% RH.

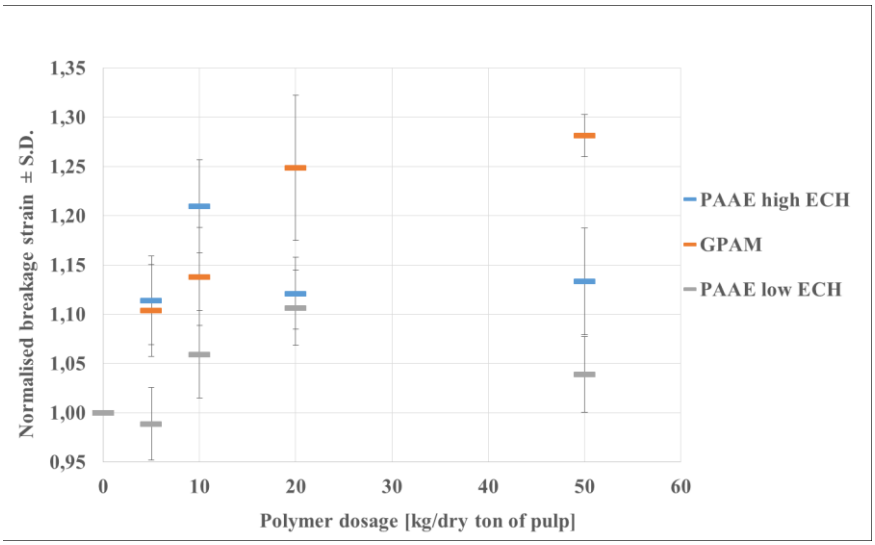


Figure 36. Effect of GPAM and PAAE on breakage strain of paper hand sheet at 50% RH. (Abs. breakage strain of ref. sheets: PAAE high ECH = 4.0%, GPAM = 3.9% and PAAE low ECH = 4.2%)

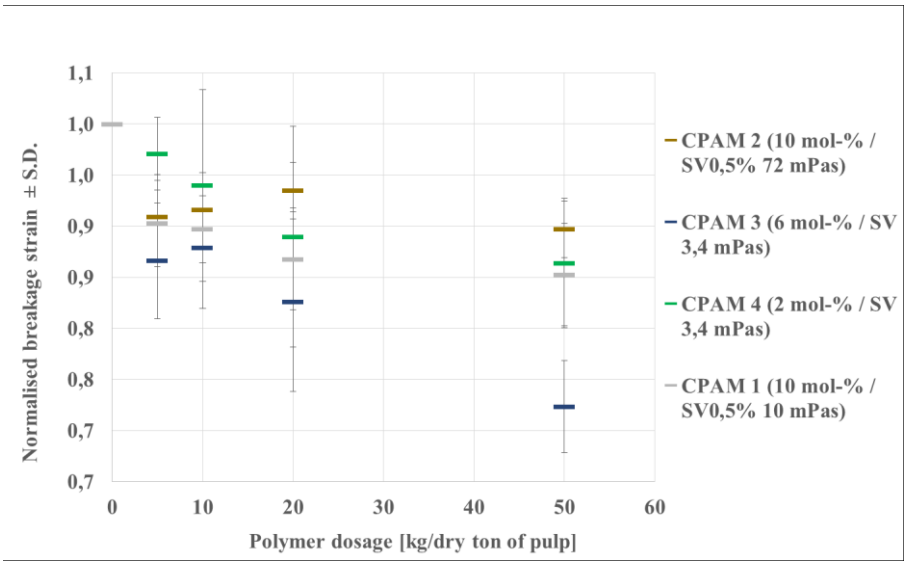


Figure 37. Effect of CPAM on breakage strain of paper hand sheet at 50 % RH. (Abs. breakage strain of ref. sheets: CPAM1 = 4.2%, CPAM2 = 4.3%, CPAM3 = 4.3% and CPAM4 = 4.2%)

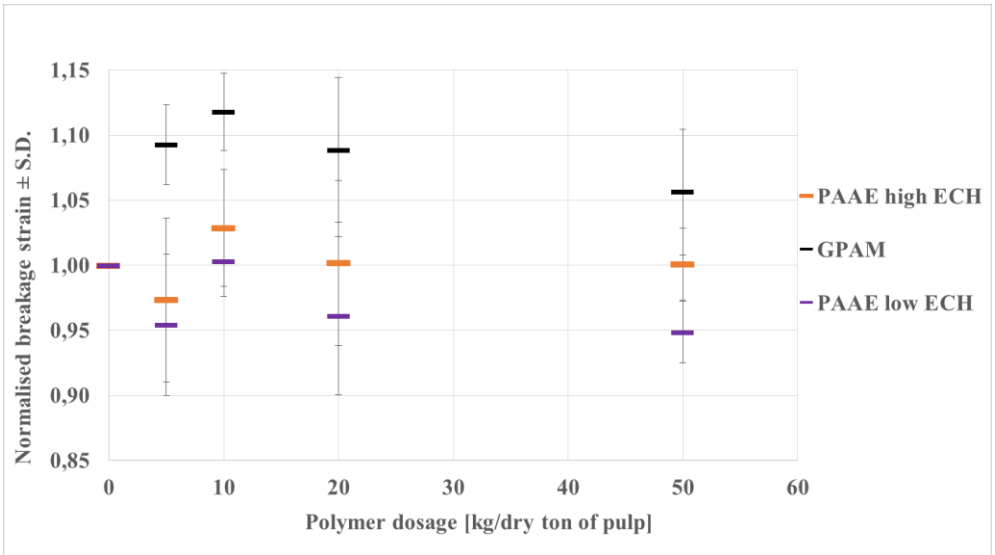


Figure 38. Effect of GPAM and PAAE on breakage strain of paper hand sheet at 80% RH. (Abs. breakage strain of ref. sheets: PAAE high ECH = 4.4%, GPAM = 4.4% and PAAE low ECH = 4.7%)

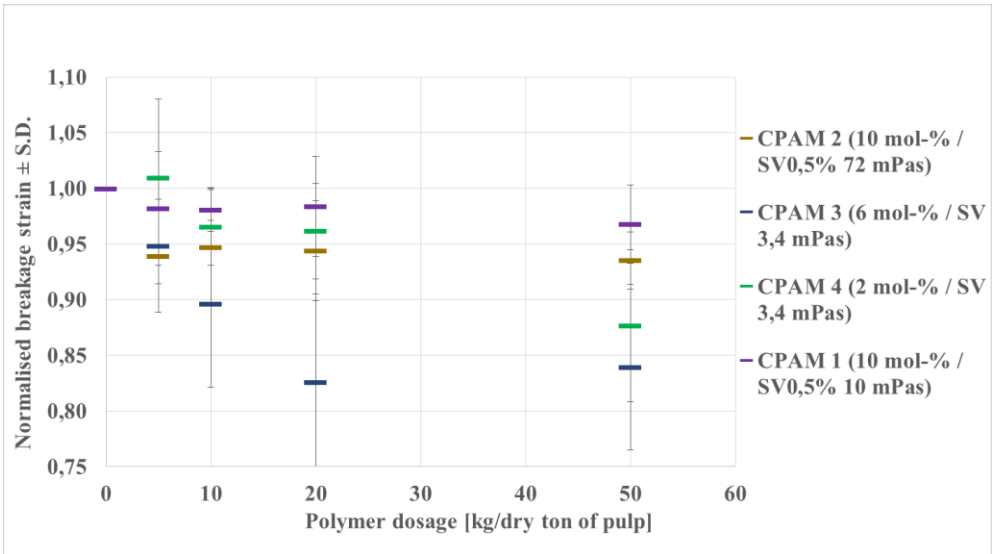


Figure 39. Effect of CPAM on breakage strain of paper hand sheet at 80 % RH. (Abs. breakage strain of ref. sheets: CPAM1 = 4.7%, CPAM2 =4.5%, CPAM3 = 4.5% and CPAM4 = 4.7%)

4.2.2 Tensile strength

Figures 40 and 42 present how GPAM and PAAE high ECH increased the tensile index and strength significantly with all of the dosages that were tested and CPAM 1, shown in Figures 41 and 43, with three highest dosage at both relative humidities. Other than these three polymers with the highest dosage increased the tensile index and strength significantly less than GPAM. CPAM 3 and CPAM 4 were the only polymers that did

not significantly increase the tensile index and strength with any of the dosages that were tested.

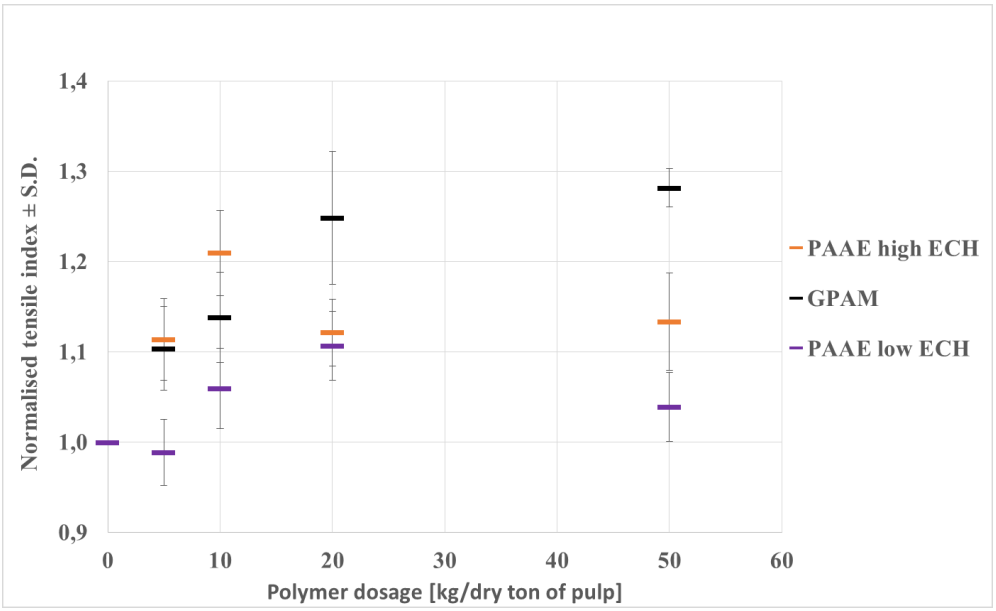


Figure 4021. Effect of GPAM and PAAE on tensile index of paper hand sheet at 50% RH. (Abs. tensile index of ref. sheets: PAAE high ECH = 67.7 Nm/g, GPAM = 74.7 Nm/g and PAAE low ECH = 71.3 Nm/g)

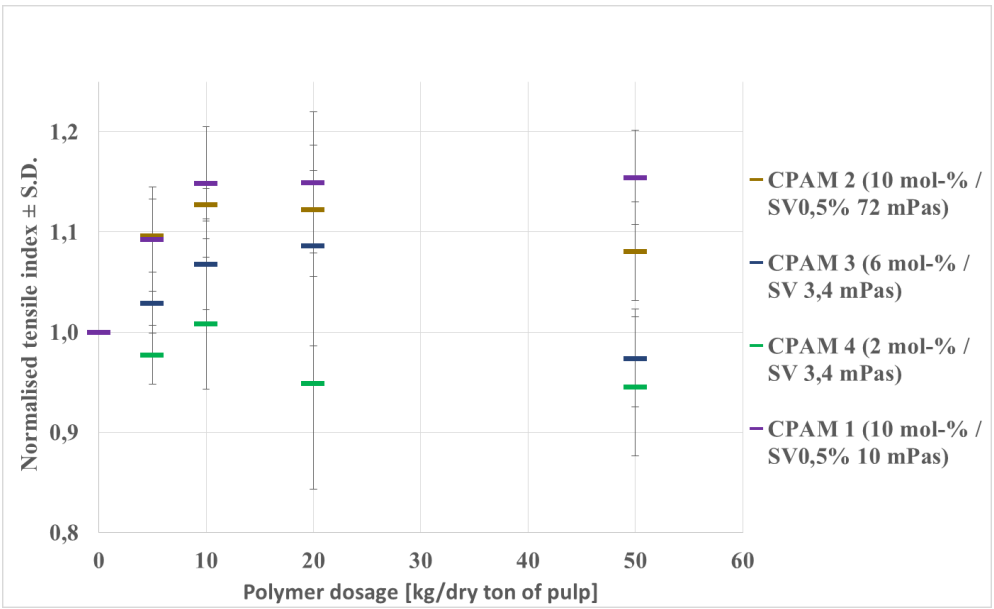


Figure 41. Effect of GPAM and PAAE on tensile index of paper hand sheet at 50% RH. (Abs. breakage strain of ref. sheets: CPAM1 = 71.3 Nm/g, CPAM2 = 69.7 Nm/g, CPAM3 = 69.7 Nm/g and CPAM4 = 72.1 Nm/g)

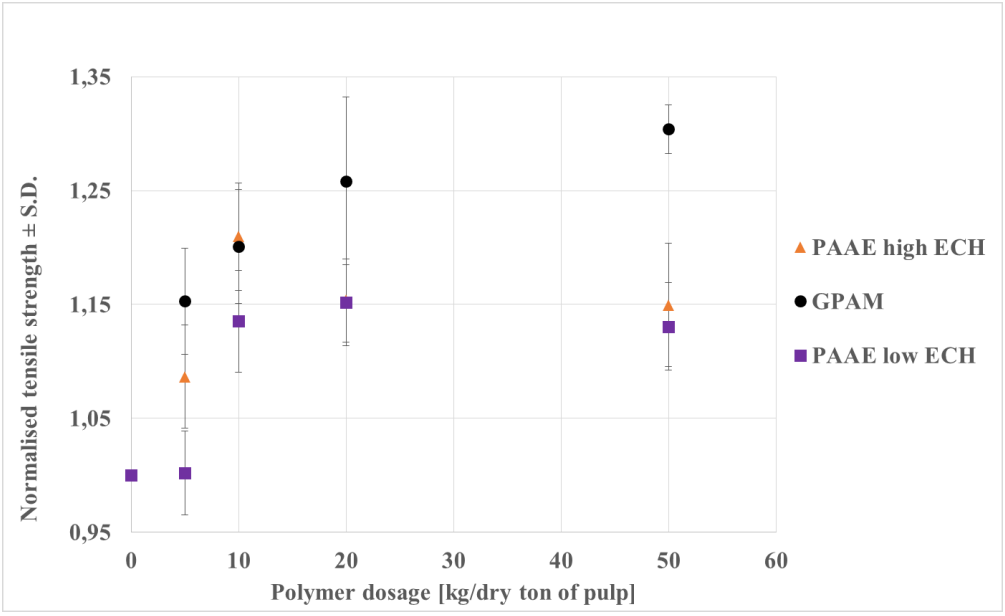


Figure 42. Effect of CPAM on tensile index of paper hand sheet at 80% RH. (Abs. tensile strength of ref. sheets: PAAE high ECH = 7.3 kN/m, GPAM = 7.9 kN/m and PAAE low ECH = 7.3 kN/m)

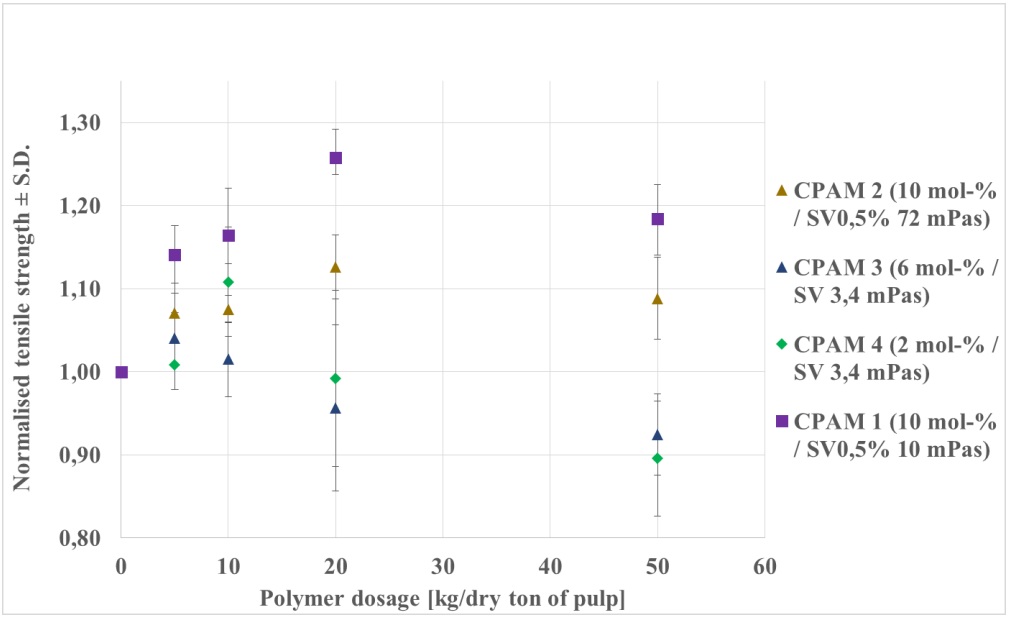


Figure 43. Effect of CPAM on tensile index of paper hand sheet at 80% RH. (Abs. tensile strength of ref. sheets: CPAM1 = 7.3 kN/m, CPAM2 = 7.5 kN/m, CPAM3 = 7.5 kN/m and CPAM4 = 7.8 kN/m)

4.2.3 Hand sheet formation

CPAM 2 improved the beta-formation significantly with all of the dosages that were tested. PAAE high ECH and CPAM 3 improved the beta-formation with the three highest dosages. GPAM and all the polymers mentioned earlier showed approximately

equal performance with the highest dosage. CPAM 4 significantly impaired the beta-formation with all of the dosages that were tested, as can be seen from Figures 44 and 45.

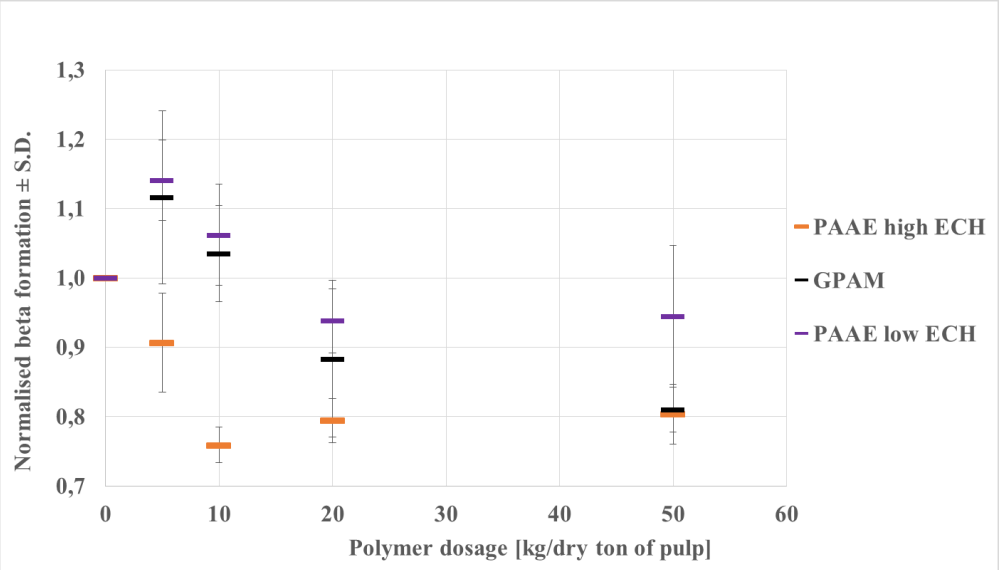


Figure 44. Effect of GPAM and PAAE on beta-formation of paper hand sheet at 50% RH. (Abs. beta-formation of ref. sheets: PAAE high ECH = 6.8, GPAM = 6.1 and PAAE low ECH = 6.0)

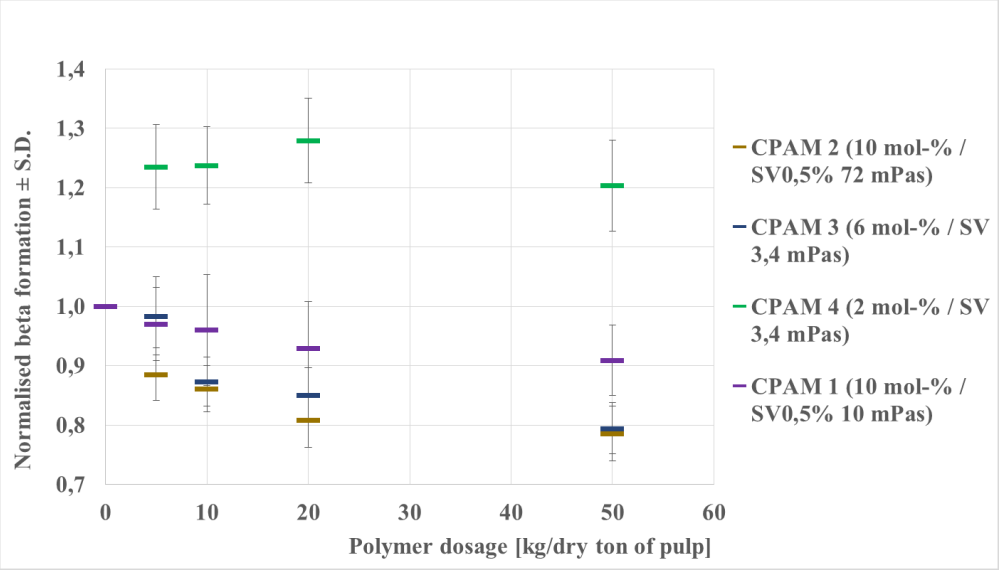


Figure 45. Effect of CPAM on beta-formation of paper hand sheet at 50% RH. (Abs. beta-formation of ref. sheets: CPAM1 = 6.0, CPAM2 = 6.0, CPAM3 = 6.0 and CPAM4 = 6.1)

4.2.4 Other effects

The dewatering time was significantly increased with CPAM 3 (8 to 37 sec) and CPAM 4 (9 to 24 sec) with the three highest dosages, as can be seen from Figure 46.

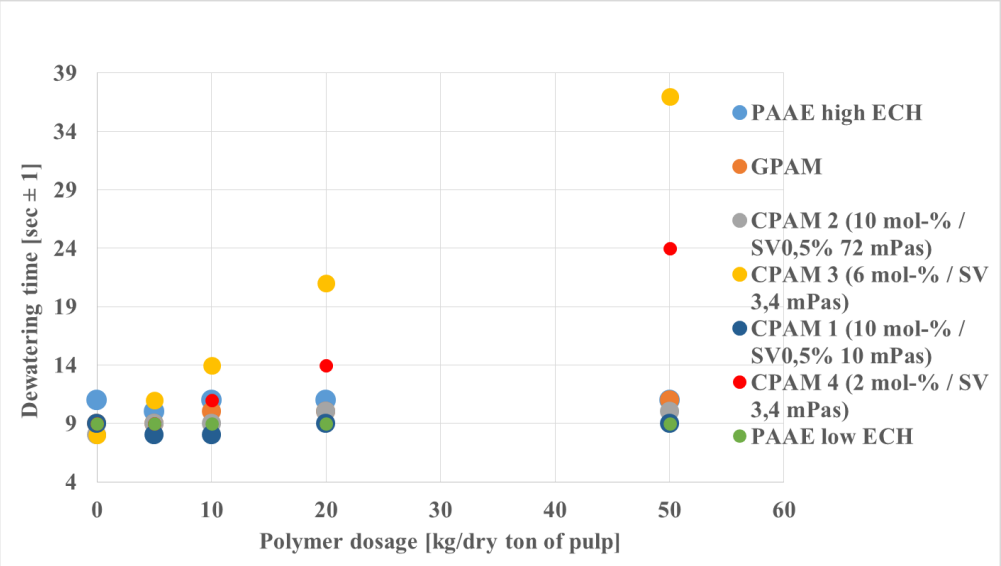


Figure 46. Effect of synthetic polymer on dewatering time in paper sheet formation.

Figure 47 shows that the elastic modulus was significantly increased by CPAM 2, CPAM 3 and PAAE low ECH with all the dosages that were tested. All the polymers that were tested increased the elastic modulus significantly at the two highest dosages except CPAM 4, which did not increase with any dosage, as can be seen from Figure 48.

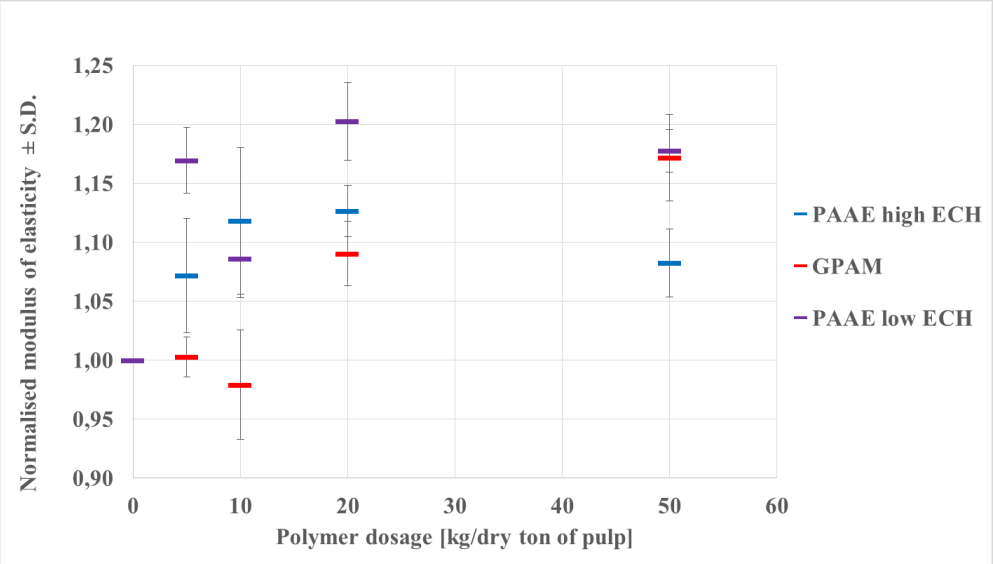


Figure 47. Effect of GPAM and PAAE on modulus of elasticity of paper hand sheet at 50% RH. (Abs. modulus of elasticity of ref. sheets: PAAE high ECH = 4.4 GPa, GPAM = 4.8 GPa and PAAE low ECH = 4.2 GPa)

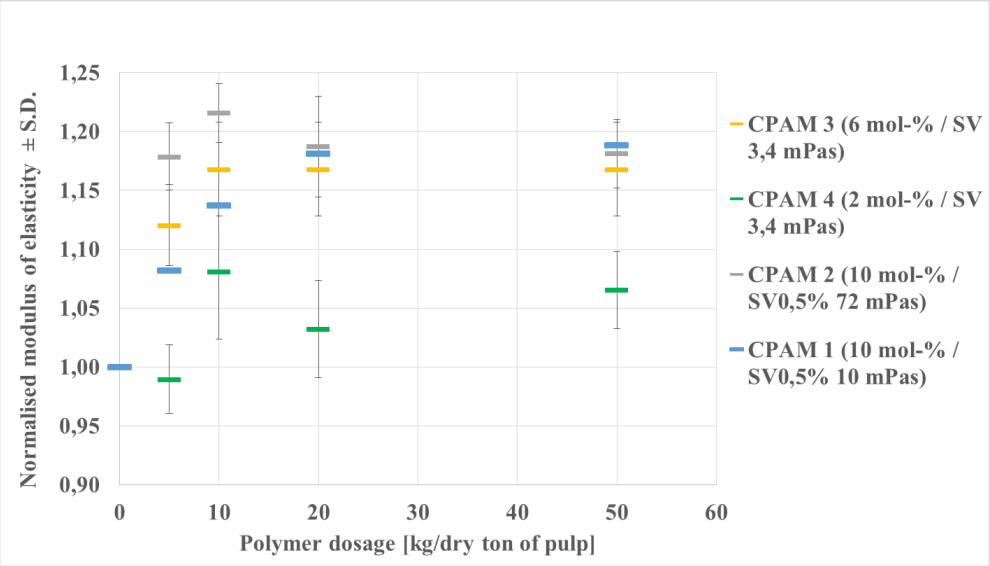


Figure 48. Effect of CPAM on modulus of elasticity of paper hand sheet at 50% RH. (Abs. modulus of elasticity of ref. sheets: CPAM1 = 4.2 GPa, CPAM2 = 4.1 GPa, CPAM3 = 4.1 GPa and CPAM4 = 4.2 GPa)

Considering all the synthetic polymers that were tested, there was no good correlation between the modulus of elasticity and density or breakage strain in paper sheets containing synthetic polymers, which can be seen from Figure 49.

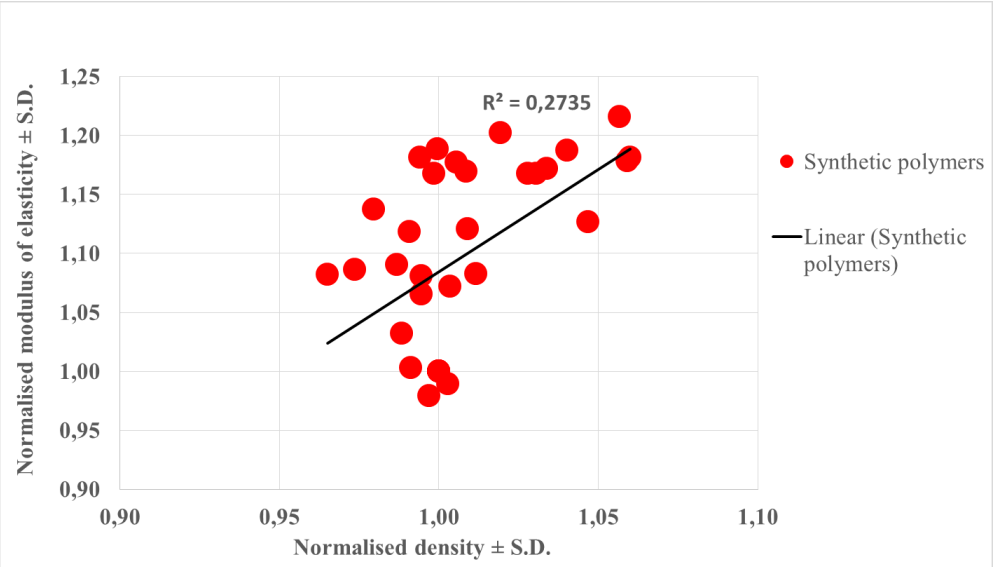


Figure 49. Effect of synthetic polymers on modulus of elasticity and density of paper hand sheet.

There was a very low correlation between the breakage strain and tensile strength at both relative humidities among all the synthetic polymers, as can be seen from Figures 50 and 51.

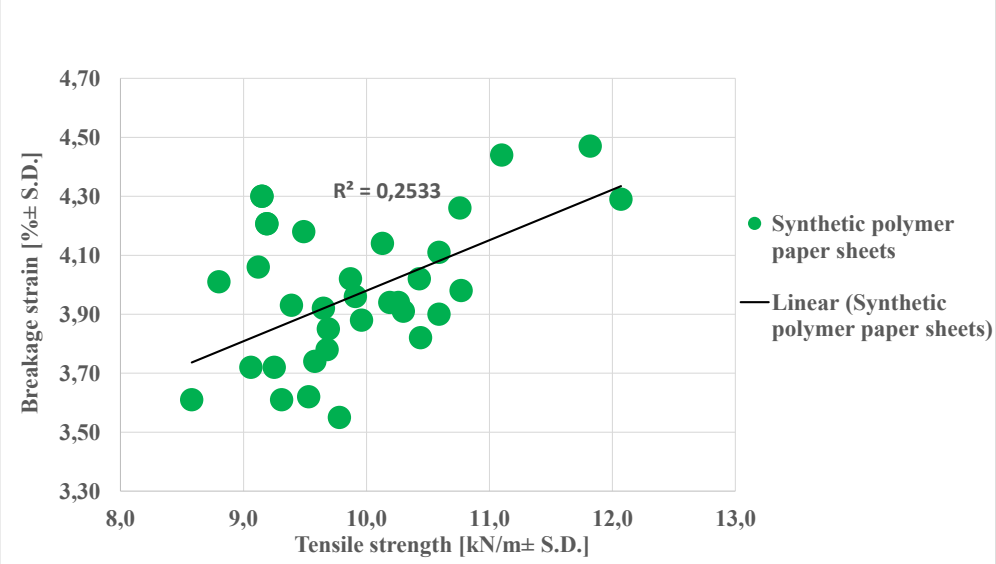


Figure 50. Effect of synthetic polymers on breakage strain and tensile strength of paper hand sheets at 50% RH.

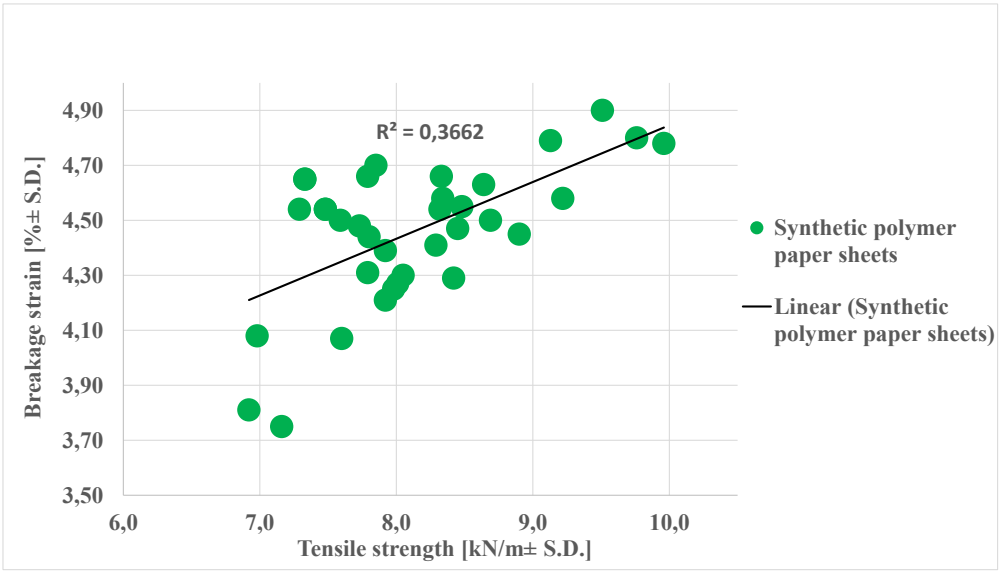


Figure 51. Effect of synthetic polymers on breakage strain and tensile strength of paper hand sheets at 80% RH.

4.3 Effect of polymer bi-layering on paper properties

The first set of tests using the bi-layering technique was performed with a polycarbonate drying plate (see Breakage strain) and the second set with this technique using a green

drying plate (see Additional tests). These two test sets are not comparable with each other.

4.3.1 Breakage strain

The addition of GPAM + CMC HMW (50% + 50%) was the only polymer combination that increased the breakage strain significantly at both relative humidities, as can be seen from Figures 52 and 53. However, the combination of GPAM + CMC HMW (50% + 50%) increased the breakage strain significantly more only in comparison to the combinations of cationic NFC + PLA (50% + 50%) and PAH + HA (20% + 80%) with 20 kg/t of dry pulp at both relative humidities. With a pulp dosage of 50 kg/t the combination GPAM + CMC HMW (50% + 50%) increased the breakage strain significantly more compared to NFC + PLA (50% + 50%) at 80% RH and PAH + HA (20% + 80%) at 50% RH. There was no significant difference in the breakage strain between GPAM + CMC HMW (50% + 50%) and PAAE high ECH + CMC HMW at any polymer dosage at either relative humidity.

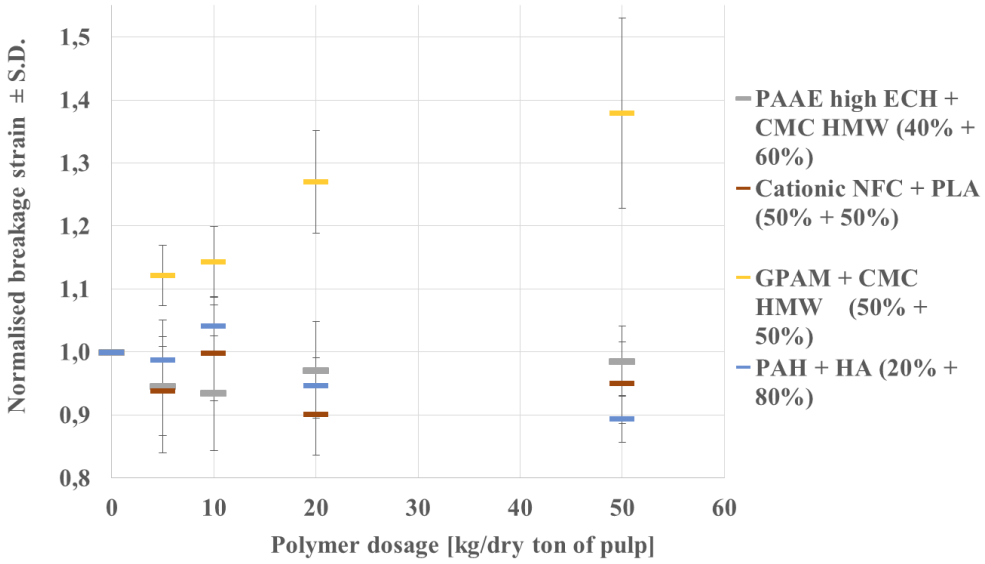


Figure 52. Effect of polymer bi-layering of fibers on breakage strain of paper hand sheet at 50% RH. (Abs. breakage strain of ref. sheets: PAAE+CMC HMW = 4.0%, Cat. NFC+PLA = 3.9%, GPAM+CMC HMW = 4.0% and PAH+HA = 4.0%)

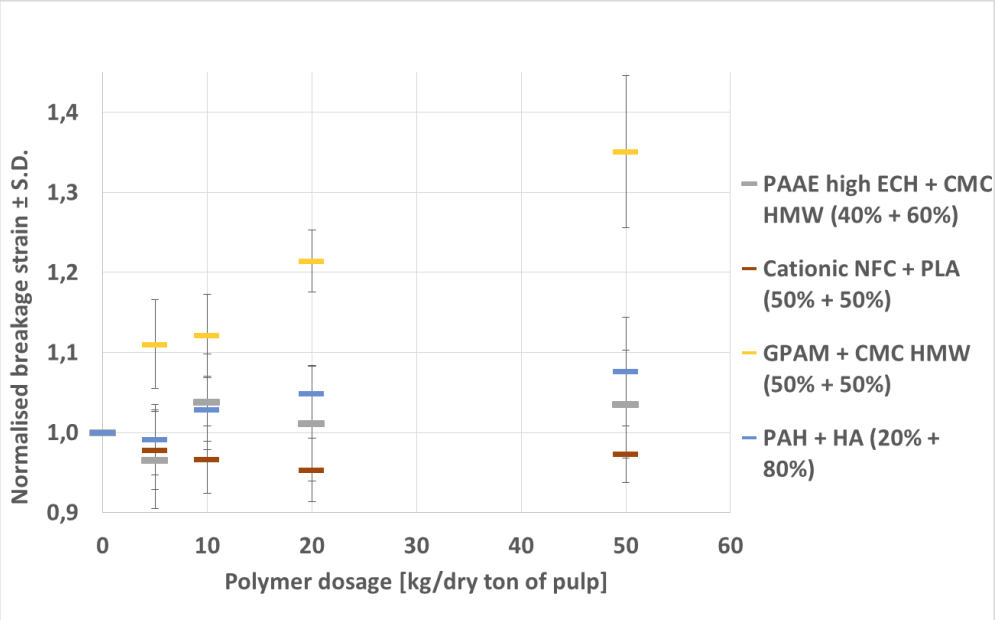


Figure 53. Effect of polymer bi-layering of fibers on breakage strain of paper hand sheet at 80% RH. (Abs. breakage strain of ref. sheets: PAAE+CMC HMW = 4.5%, Cat. NFC+PLA = 4.4%, GPAM+CMC HMW = 4.5% and PAH+HA = 4.5%)

4.3.2 Tensile strength

At both relative humidities that were tested the combinations GPAM + CMC HMW (50% + 50%) and PAH + HA (20% + 80%) both increased the tensile index and strength significantly with all the dosages that were tested. The same was observed when PAAE high ECH + CMC HMW were combined at the three highest dosages (10, 20 and 50 kg/t). Combining cationic NFC + PLA (50% + 50%) did not show any significant effects on the tensile index at either relative humidity. Cationic NFC + PLA gave a significantly lower tensile index with the two highest dosages at 80% RH but at 50% RH the difference was no longer significant when compared with the other polymer combinations. The data in Figures 54-55 illustrate the tensile indices and strength as a function of the polymer dosage.

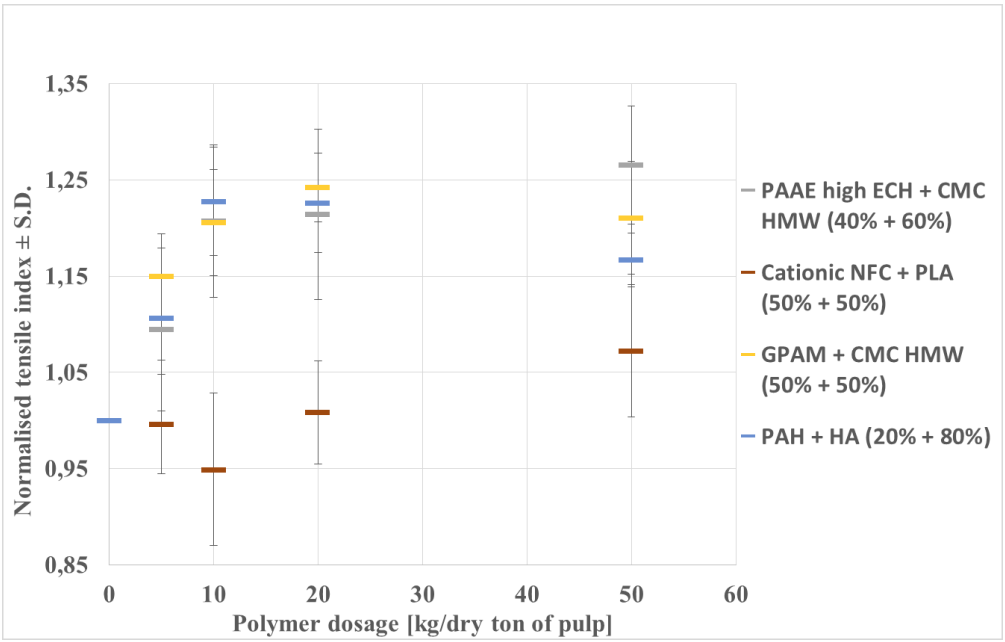


Figure 54. Effect of polymer bi-layering of fibers on tensile index of paper hand sheet at 50% RH. (Abs. tensile index of ref. sheets: PAAE+CMC HMW = 68.0 Nm/g Cat. NFC+PLA = 74.7 Nm/g, GPAM+CMC HMW = 66.6 Nm/g and PAH+HA = 66.6 Nm/g)

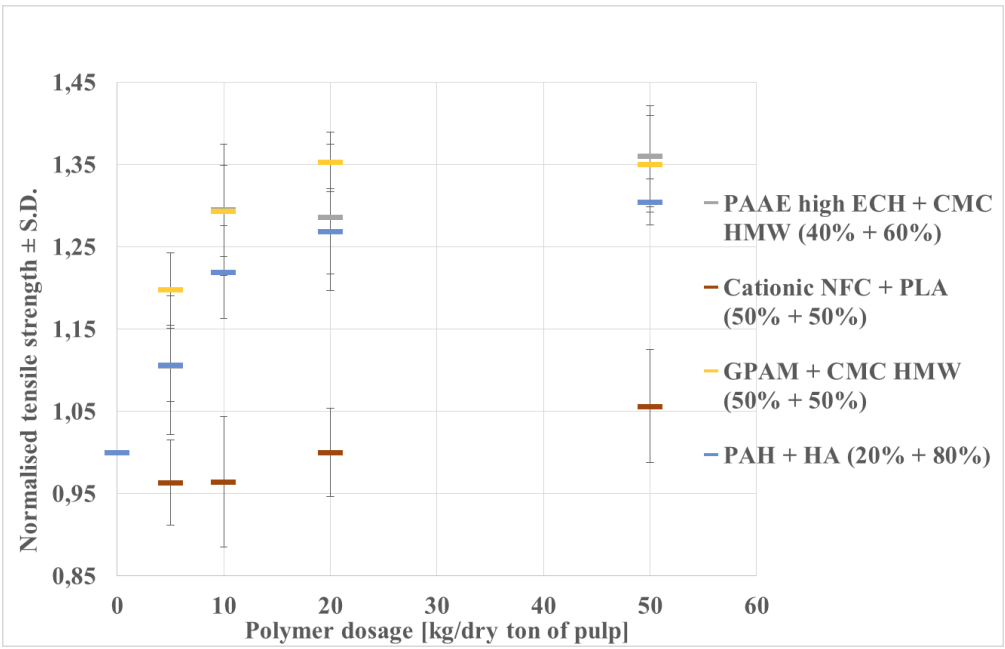


Figure 55. Effect of polymer bi-layering of fibers on tensile strength of paper hand sheet at 80% RH. (Abs. tensile strength of ref. sheets: PAAE+CMC HMW = 7.3 kN/m Cat. NFC+PLA = 7.9 kN/m, GPAM+CMC HMW = 7.1 kN/m and PAH+HA = 7.1 kN/m)

4.3.3 Hand sheet formation

There were no significant differences in beta-formation between the polymer combinations that were tested at the three lowest dosages, as can be seen from Figure

56. The combination of GPAM + HMW CMC improved the beta-formation at the two lowest dosages. At the highest dosage this combination again impaired the beta-formation, which was significantly lower than in any other combination, which all improved the beta-formation at the highest dosage.

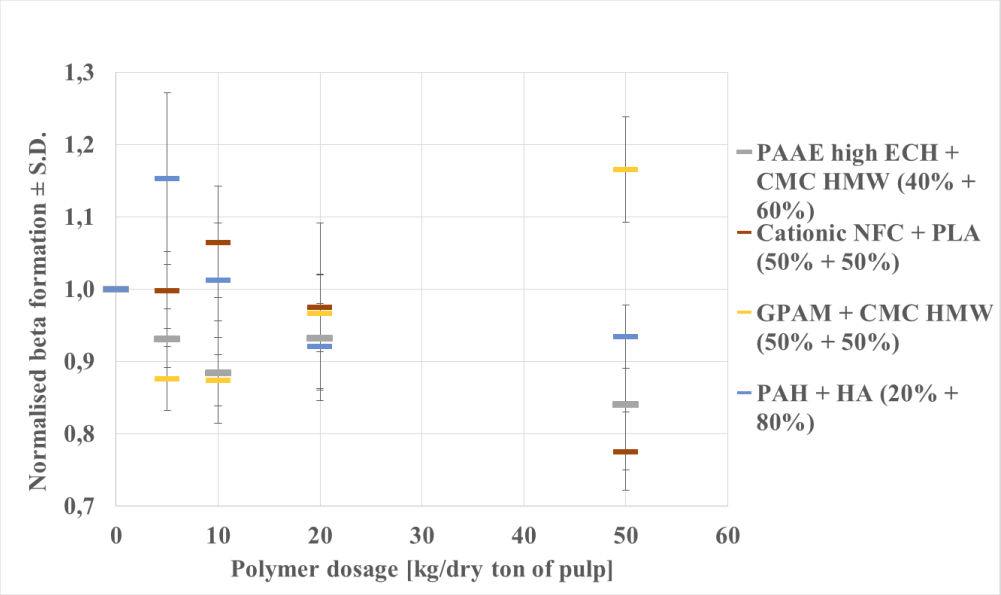
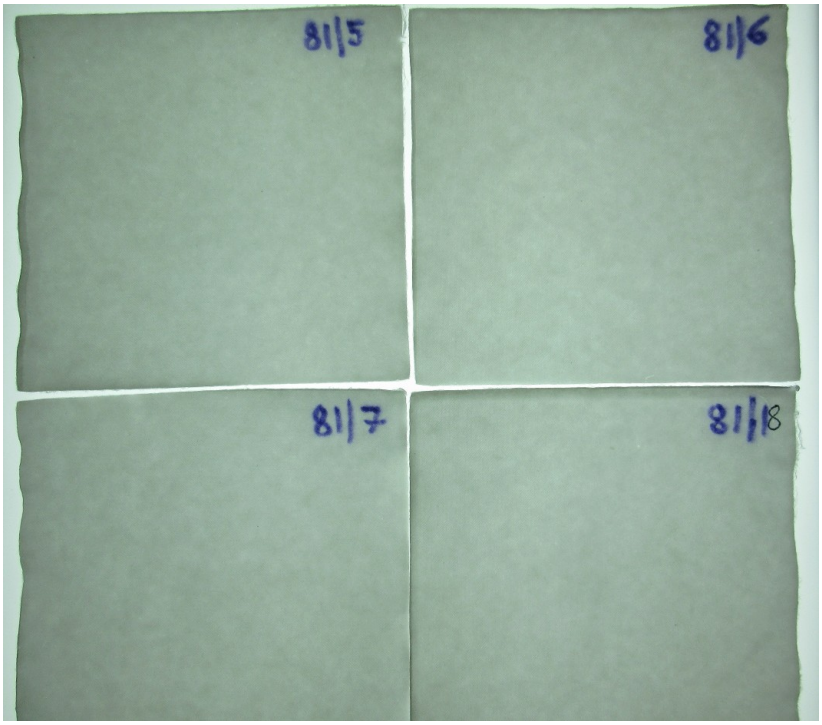


Figure 56. Effect of polymer bi-layering of fibers on beta-formation of paper hand sheet at 50% RH. (Abs. beta-formation of ref. sheets: PAAE+CMC HMW = 6.8 Cat. NFC+PLA = 6.1, GPAM+CMC HMW = 6.0 and PAH+HA = 6.0)

4.3.4 Other effects

When combining GPAM + HMW CMC (50% + 50%) the waviness and drying shrinkage of the paperboard sheets increased with the dosage as shown by visual observations. On the other hand, the breakage also increased with the dosage. Picture 4 shows shrunken and wavy paperboard sheets prepared with a 50 kg/t dosage of GPAM + HMW CMC (50% + 50%), which gave the highest measured breakage strain values in this work, 5.5% at 50% RH and 6.0% at 80% RH.



Picture 4. Shrunken and wavy (can be seen from the edges) paperboard sheets.

A high level of drying shrinkage could explain at least part of the higher breakage strain values achieved with this polymer combination. In order to find out whether the higher breakage strain was caused by a higher drying shrinkage, increasing dosage or an unsuitable selection of drying plate material, the most relevant polymers/those with the greatest potential (cationic starch, GPAM and GPAM + HMW CMC (50% + 50%) with a dosage of 50 kg/t added to the dry pulp were retested (tests 88 and 90-92) using green drying plates and a suction board instead of polycarbonate drying plates and a wire screen for wet pressing and drying. As a result, drying shrinkage was no longer visually observed in the paper sheets containing HMW CMC (50% + 50%) when they were dried with green plates. Moreover, the results showed that there was no significant difference in the tensile index and breakage strain between the paper sheets when they were prepared with green drying plates and suction boards. The results also showed that the standard deviation was generally higher when polycarbonate drying plates were used in the drying. Figures 57 and 58 show that there was a moderate correlation between the breakage strain and tensile strength with the polymer combination GPAM + CMC HMW (50%+50%) at both relative humidities and PAH + HA (80%+20%) at 80% RH.

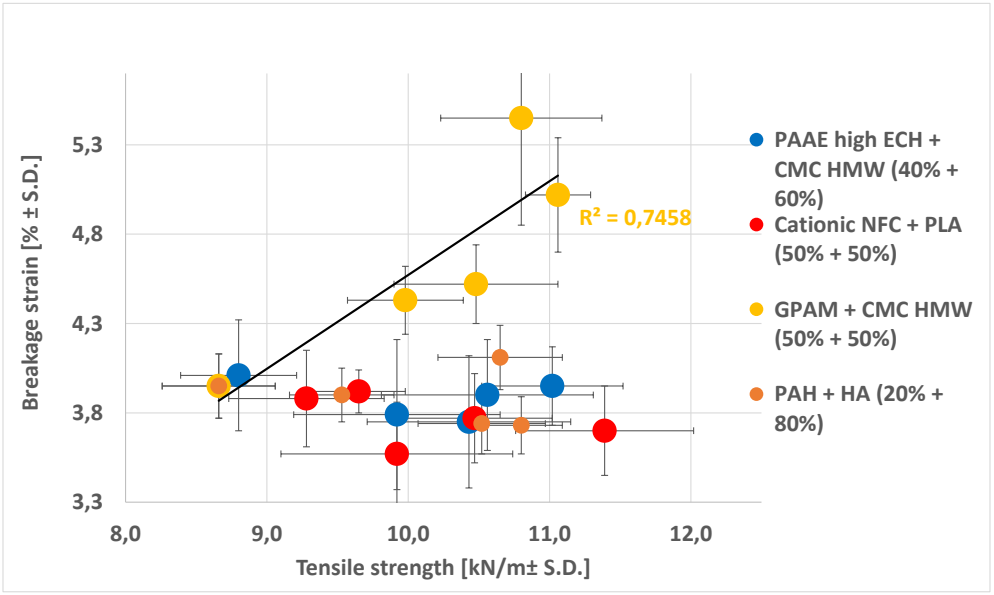


Figure 57. Effect of polymer bi-layering on breakage strain and tensile strength of paper hand sheet at 50% RH.

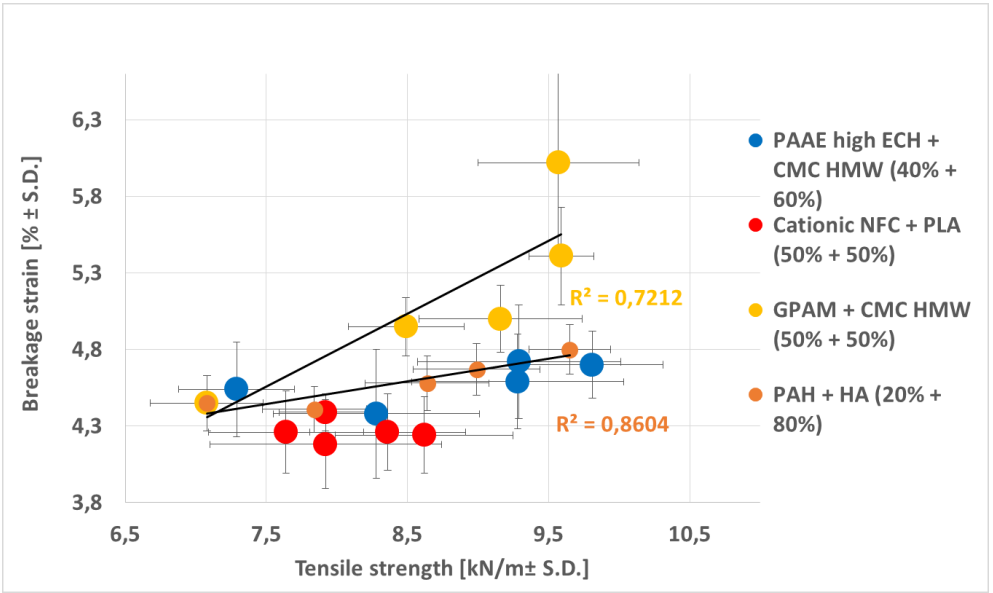


Figure 58. Effect of polymer bi-layering on breakage strain and tensile strength of paper hand sheet at 80% RH.

Figure 59 shows that the polymer combinations PAAE high ECH + CMC HMW (40% + 60%) and PAH + HA (20% + 80%) significantly increased the modulus of elasticity at dosages of 10, 20 and 50 kg/t at 50% RH.

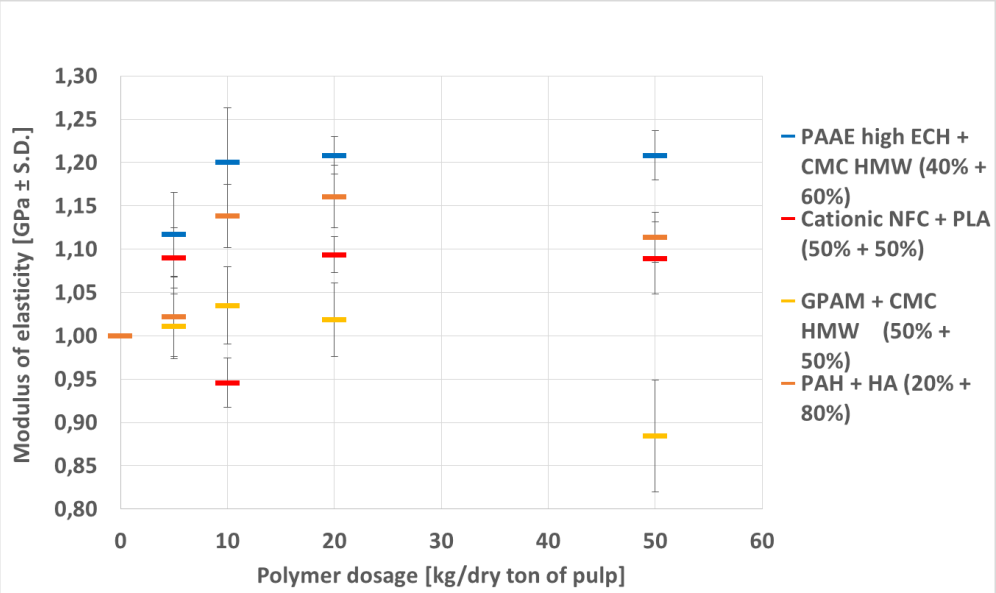


Figure 59. Effect of polymer bi-layering on modulus of elasticity of paper hand sheet at 50% RH. (Abs. beta-formation of ref. sheets: PAAE+CMC HMW = 6.8 Cat. NFC+PLA = 6.1, GPAM+CMC HMW = 6.0 and PAH+HA = 6.0)

4.4 Additional tests

As previously shown, the combination GPAM + CMC HMW (50% + 50%) was the only breakage strain that increased significantly at both relative humidities. Hence, different ratios between GPAM and CMC HMW were considered worth testing, as well as the ratio giving the highest breakage strain but with a CMC of lower molecular weight and applying the same polymer ratios. Additionally, because of the potential of CPAM 2 for good beta-formation it was considered worth testing together with the best-performing CMC grade.

The results of the additional tests showed that only the combinations GPAM + CMC HMW (25% + 75%) and GPAM + CMC LMW (25% + 75%) significantly increased the tensile index at every dosage when tested at 50% RH, without producing any significant differences between the polymers, as can be seen from Figure 60. Combining GPAM + CMC HMW (75% + 25%) could increase the tensile index significantly at dosages of 10 and 20 kg/t. The combination GPAM + CMC HMW (50% + 50%) also showed significant improvement in the tensile index at a dosage of 50 kg/t. Since the grammage was not determined at 80% RH, the tensile strength was the only comparable result at this humidity. The data in Figure 61 show that when tested at 80% RH, all the polymers were able to increase the tensile strength significantly at dosages of 10, 20 and 50 kg/t

but the combination CPAM 2 + CMC LMW (25% + 75%) only with dosages of 20 and 50 kg/t.

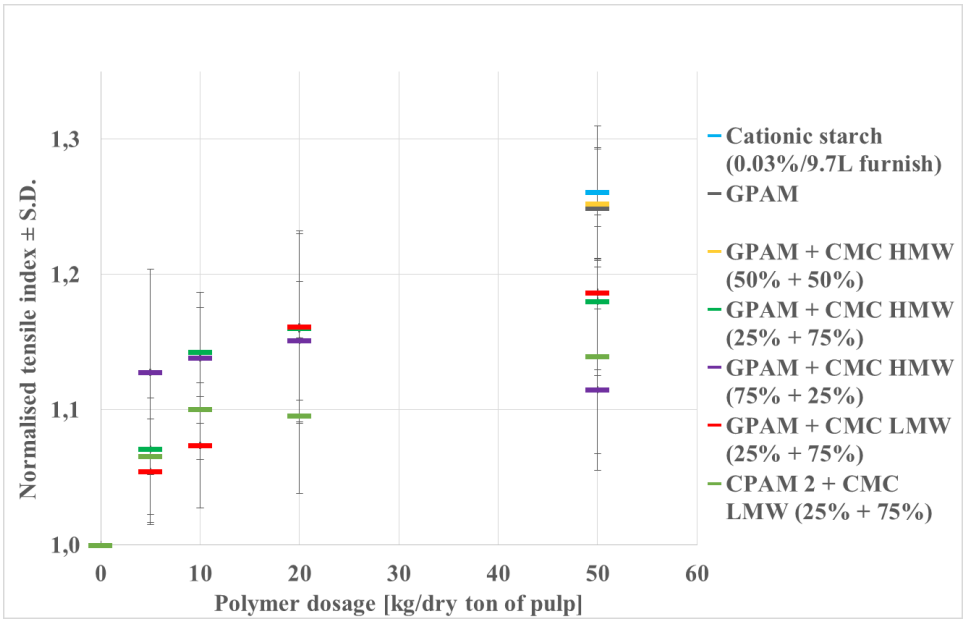


Figure 60. Effect of polymer bi-layering of fibers with GPAM and CMC on tensile index of paper hand sheet at 50% RH. (Cationic starch, GPAM and GPA + CMC HMW (50% + 50%) were only tested with a 50 kg/t dosage as references).

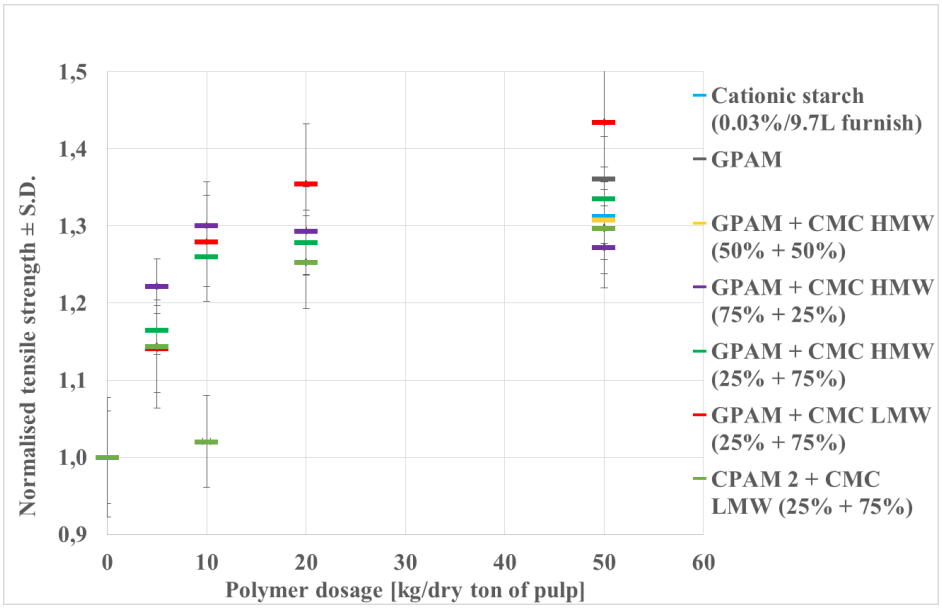


Figure 61. Effect of polymer bi-layering of fibers with GPAM and CMC on tensile strength of paper hand sheet at 80% RH.

The breakage strain increased significantly with the use of the combination GPAM + CMC LMW (25% + 75%) at dosages of 5, 20 and 50 kg/t and with CPAM 2 + CMC LMW (25% + 75%) at dosages of 10 and 50 kg/t when measured at 50% RH, as can be seen from Figure 62.

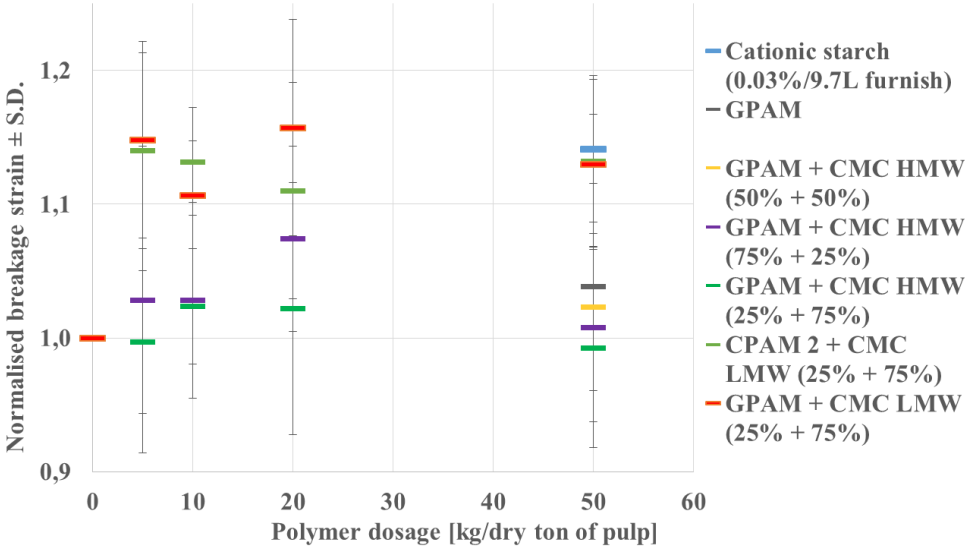


Figure 62. Effect of polymer bi-layering with GPAM and CMC on breakage strain of paper hand sheet at 50% RH.

At 80% RH the breakage strain increased significantly for every polymer combination at almost every dosage. However, there were no significant differences in the breakage strains between the polymer combinations when measured at either relative humidity, as can be seen from Figure 63.

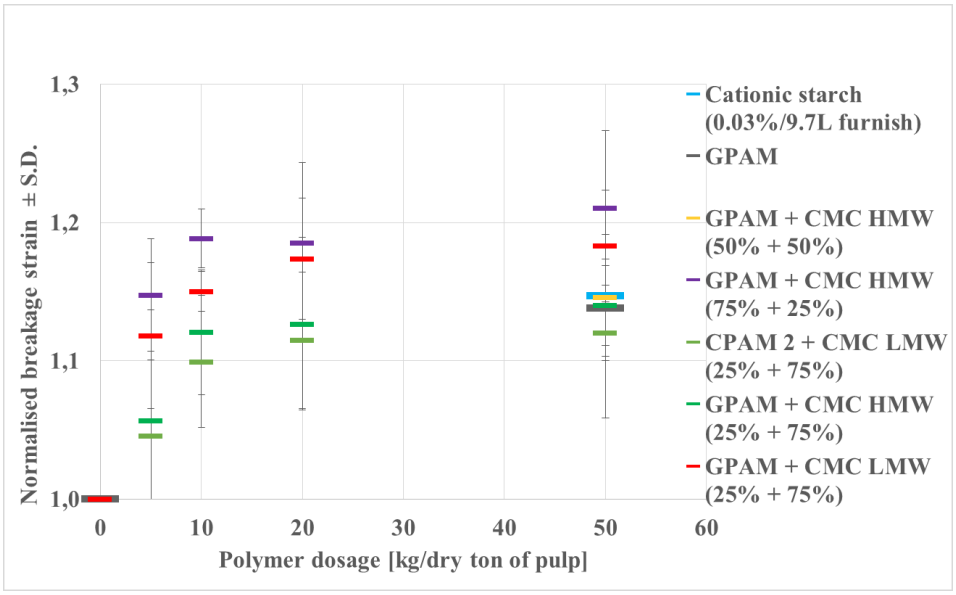


Figure 63. Effect of polymer bi-layering of fibers with GPAM and CMC on breakage strain of paper hand sheet at 80% RH.

The beta-formation was significantly improved with the combination CPAM 2 + CMC LMW (25% + 75%) at all the dosages that were tested. The combination of GPAM + CMC HMW (75% + 25%) again significantly impaired the beta-formation at increasing dosages; see Figure 64.

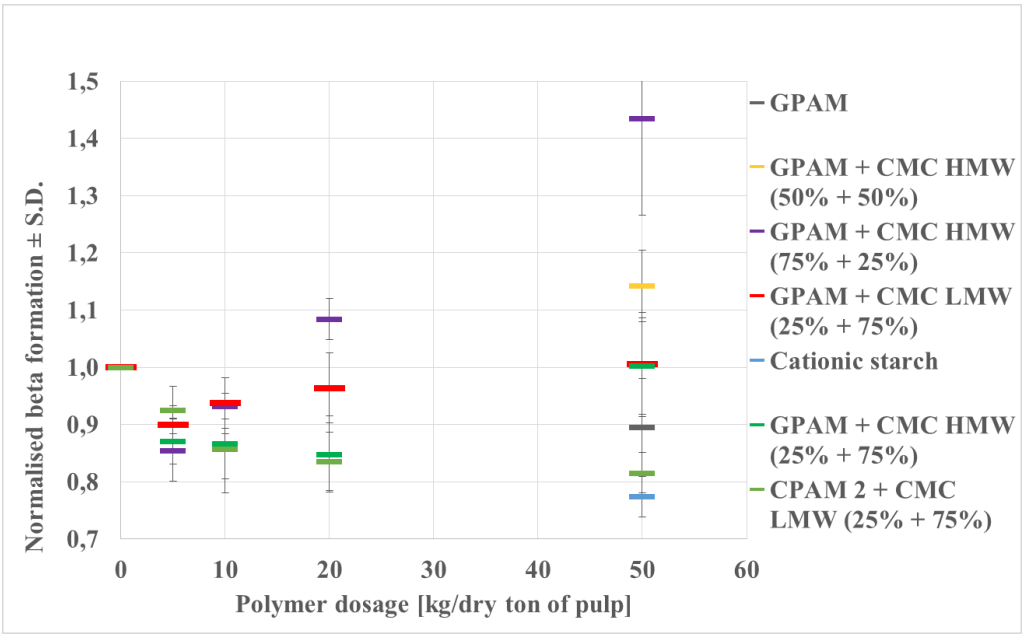


Figure 64. Effect of bi-layering of fibers with GPAM and CMC on beta-formation of paper hand sheet at 50% RH.

The data in Figure 65 indicate that the modulus of elasticity could be significantly increased with the combination GPAM + CMC (50% + 50%) at a dosage of 50 kg/t and to some degree with a GPAM + CMC HMW (25% + 75%) polymer combination at dosages of 10 kg/t and above when determined at 50% RH.

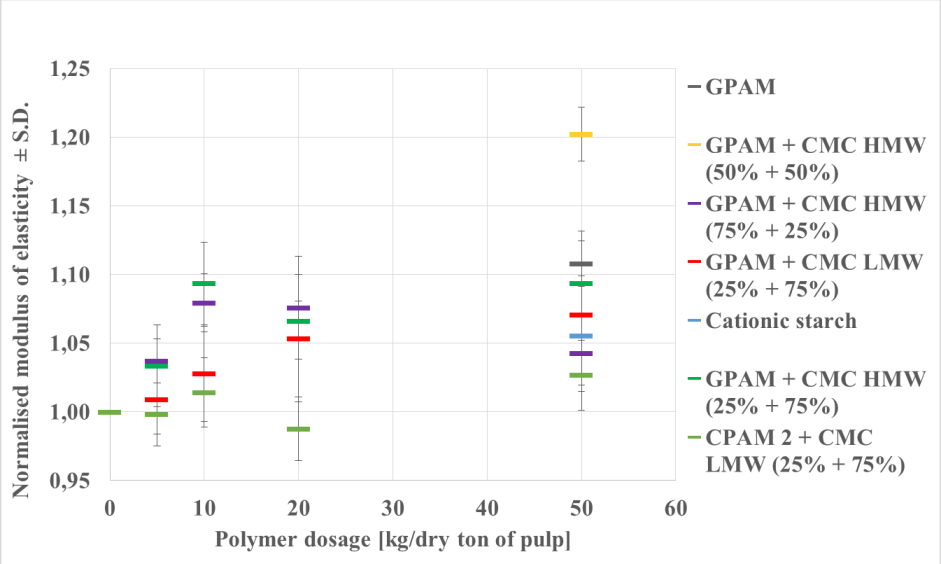


Figure 65. Effect of polymer bi-layering of fibers with GPAM and CMC on modulus of elasticity of paper hand sheet at 50% RH

Figures 66 and 67 show that there was a moderate correlation between the modulus of elasticity and density but no correlation with the breakage strain in paper hand sheets containing bi-layered polymer structures.

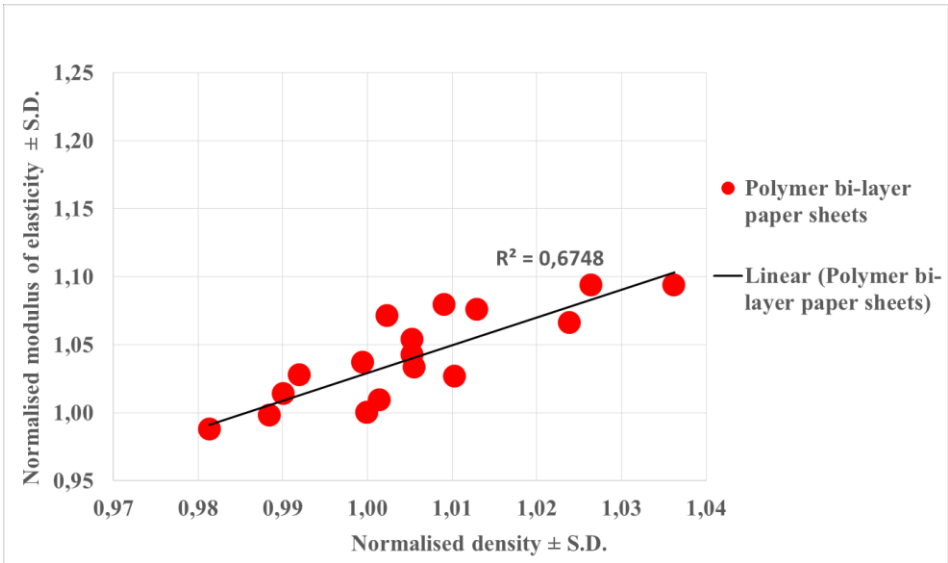


Figure 66. Effect of polymer bi-layering of fibers on modulus of elasticity and density of paper hand sheet.

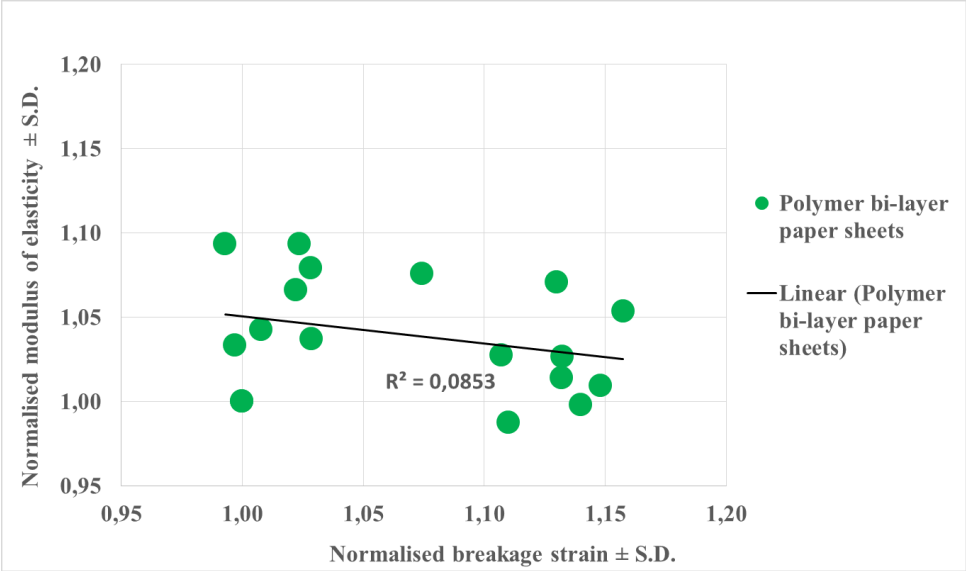


Figure 67. Effect of polymer bi-layering of fibers on modulus of elasticity and breakage strain of paper hand sheet at 50% RH.

Figure 68 shows that there was no correlation between the breakage strain and tensile strength of the polymer bi-layered paper sheets at 50% RH. At 80% RH, there was generally a good correlation between the same variables, as illustrated in Figure 69, and a very good one for each individual polymer combination, as can be seen from Figure 70. GPAM + HMW CMC (75% + 25%) showed the highest rate of development of the breakage strain, i.e., slope of the trendline, while the others showed similar development, as can be seen from Figure 70.

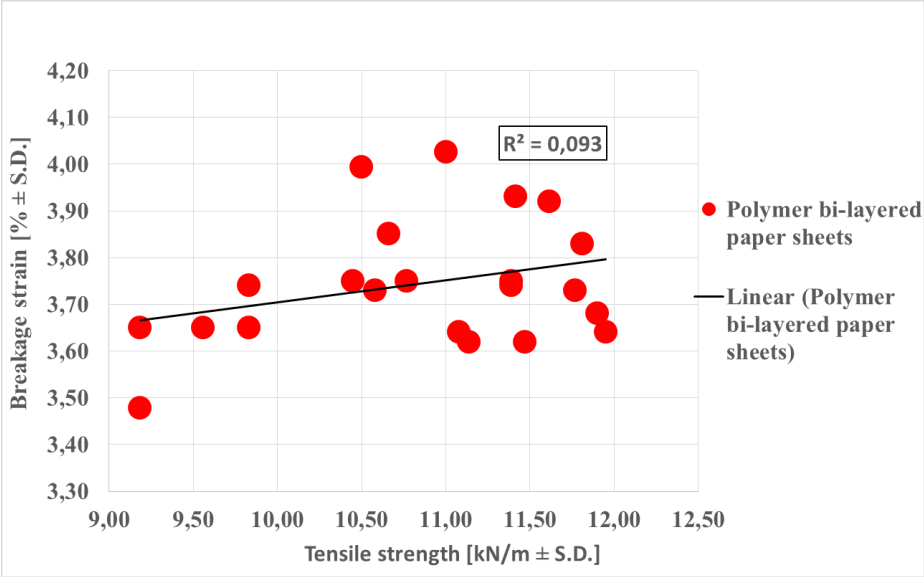


Figure 68. Effect of polymer bi-layering on breakage strain and tensile strength of paper hand sheet at 50% RH.

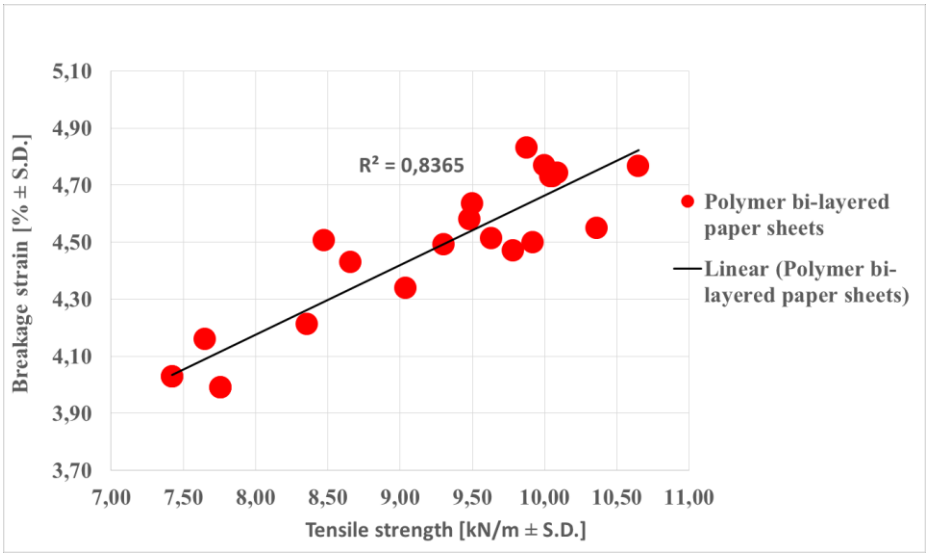


Figure 69. Effect of polymer bi-layering on breakage strain and tensile strength of paper hand sheet at 80% RH.

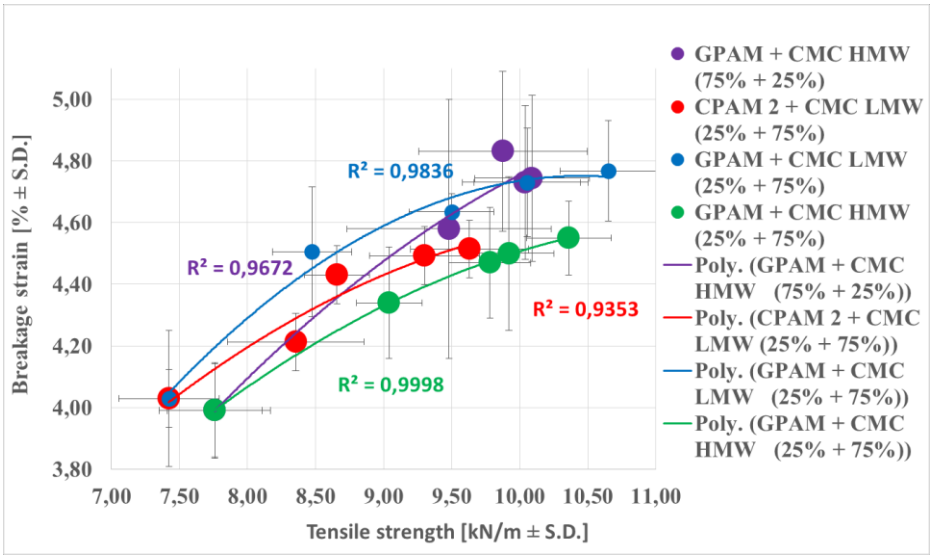


Figure 70. Effect of polymer bi-layering on breakage strain and tensile strength of paper hand sheet at 80% RH.

5 Discussion

According to the literature review, it could be expected that one way to improve the extensibility of paper is through an increase in its tensile strength. Of the natural polymers cationic NFC, cationic guar gum and chitosan should be the potential ones to increase the tensile strength of paper. However, only cationic NFC was observed to do so under the circumstances and conditions tested here. Nevertheless, neither NFC nor any other natural polymer was able significantly to increase the breakage strain of hand sheets made from beaten (SR° 25-28) kraft pulp. However, using a smaller furnish

volume, i.e., a higher stock pulp consistency, with the addition of cationic starch with a dosage up to 100 kg/t to dry pulp indicated that dosages below 50 kg/t were insufficient to bring about an increase in the breakage strain, irrespective of the relative humidity in testing. This was in line with what was reported in the literature review. This indicated that the polymer dosage needed to significantly increase the extensibility of the paper in terms of breakage strain, is more probably hundreds of kilos of polymer per dry ton of pulp. On the other hand, a significant increase in the breakage strain with the addition of a dosage of 100 kg/t to the dry pulp could also, at least partly, be due to the higher stock consistency in forming. This is also known to impact on the fiber orientation by increasing the number of fibers aligned in the z-direction in a paper sheet. This may affect the breakage strain of the paper positively and one reason for that could be the higher strain potential of the fibers in the cross direction than in the axial one. Another reason could be more even local stress and strain distribution within the paper sheet.

On the basis of the pre-tests, dry pulp polymer dosages of 100 kg/t and beyond were excluded on the basis of the poor dewatering rates in forming, as well as because of wet-pressing issues with detaching the sheet after drying. All of the natural polymers that were tested except chitosan in adipic acid significantly improved the beta-formation, at least with the highest dosage. Cationic NFC, cationic guar gum and cationic starch significantly increased the elastic modulus of the paper. Chitosan LMW in 0.24% adipic acid at dosages of 5, 10 and 20 kg/t and in 2% citric acid at dosages of 20 and 50 kg/t also increased the elastic modulus significantly.

The literature review suggested that synthetic polymers such as GPAM, PAAE and at least high-charge density and/or high-molecular weight CPAMs were expected to increase the tensile strength and therefore also to be potential candidates for improvement of the breakage strain. This finding from the literature review regarding tensile strength was confirmed by the results presented in this study. However, only GPAM showed a significant improvement in the breakage strain at both relative humidities, but only with a dosage of 10 kg/t of dry pulp, at which the beta-formation was at its optimum. High cationic charge-density CPAMs improved the beta-formation significantly at the highest dosage, which was not expected on the basis of the literature review. A possible explanation is that the high-shear mixing (90 sec/2000 rpm) after the addition of the polymer broke the flocs, which were subsequently dispersed and did not

reflocculate back to the same extent. The highest increase in the dewatering time in all the tests was observed for CPAM 3 (8 to 37 sec) and CPAM 4 (9 to 24 sec).

The literature review suggested that as the dosage of cationic strength additive increases, the surfaces of the fibers and fines typically become saturated with the addition of about 2% to the dry pulp. Above dosages of 2%, increasing flocculation often takes place, causing impaired formation of the uniformity of the paper sheets /105,106,107/. This could not be generally proven on the basis of the observed results. The observed improvement in the beta-formation at a dosage of 50 kg/t was 27% for cationic starch and between 21 and 26% for cationic NFC, cationic guar gum, CPAM 2, CPAM 3 and CPAM 4.

On the basis of the literature review, the bi- or multilayering of cellulosic fibers sequentially with cationic and anionic polymers could significantly increase the strength and/or breakage strain of paperboard. Combining PAAE together with an anionic polymer such as CMC, PAH + HA or CPAM + PLA was suggested by sources in the literature as a potential route towards higher breakage strains. As discovered earlier from the results of the current work, GPAM was the only polymer that increased breakage when applied alone. Therefore, GPAM was also tested together with a CMC. CPAM 2 was also tested together with a CMC because of its potential for enhancing the beta-formation. Cationic NFC was tested together with PLA because this provided good formation and was the only natural polymer that could increase the tensile strength. The results confirmed the literature findings, although determined at 50% RH the combinations of GPAM + CMC LMW (25% + 75%) at dosages of 5, 20 and 50 kg/t and CPAM 2 + CMC LMW (25% + 75%) at dosages of 10 and 50 kg/t were the only recipes that could significantly increase the breakage strain. Although there were no significant differences in the breakage strains between the polymer combinations at either relative humidity, one of the most interesting results was the following. When determined at 80% RH, the breakage strain was observed to be significant with every polymer combination at almost every dosage. This result confirmed the importance of moisture when increasing the strain level of paperboard with a polymer bi-layering technique. Another result that indicated the importance of moisture, i.e., plasticizer, was the relatively good correlation (R^2 = 0.84) between the breakage strain and tensile

strength of GPAM + CMC and CPAM + CMC bi-layered paper hand sheets at 80% RH. At 50% RH, this correlation was not observed.

Paper sheet containing fibers treated with GPAM + CMC LMW (25% + 75%) showed good strength properties and breakage strain at both relative humidities, unlike the other polymers, excluding those polymers which were only tested with one comparable dosage. One piece of evidence that might explain this could be the relatively good and clearly least-changing beta-formation of this polymer combination. Although GPAM + CMC HMW (75% + 25%) showed a slightly better performance than GPAM + CMC LMW (25% + 75%) as a trend in the breakage strain at 80% RH and even significantly better with 10 kg/t than cationic starch with 50 kg/t, it is worth pointing out that this happened with a GPAM dosage that was three times higher. On the other hand, more information about the retention of the polymers would be needed, but it was not measured in this work. The GPAM + CMC HMW (75% + 25%) polymer combination showed the highest development rate of the breakage strain (Figure 70) with respect to tensile strength but the difference was not significant when compared to other polymer combinations.

If the two breakage strain results that are furthest from the average of eight measurements are removed from the data, the following takes place. GPAM + CMC HMW (75% + 25%) is then the only polymer or polymer combination in this work that yields a significantly higher breakage strain than cationic starch, but only at 80% RH. However, this is only the case with a 10 kg/t dosage of GPAM + CMC HMW (75% + 25%) against a 50 kg/t dosage of cationic starch, as can be seen from Figure 42. Higher dosages of GPAM + CMC HMW (75% + 25%) caused impaired beta-formation, which probably increased the standard deviation and lowered the significance of the difference against cationic starch in terms of breakage strain. On the other hand, the cationic starch was not tested with a 10 kg/t dosage under comparable circumstances and earlier results in this thesis indicated that cationic starch probably produced a higher beta-formation with a 10 kg/t dosage. Further testing with a higher number of parallel samples would be needed to judge whether the difference in the breakage strain was significant or not when GPAM + CMC HMW (75% + 25%) and cationic starch were compared.

GPAM alone was only comparably tested (additional tests) with the GPAM + CMC and CPAM + CMC polymer combinations with a 50 kg/t dosage and therefore, the addition of CMC did not significantly improve the effect of GPAM on the breakage strain or tensile strength of a paper hand sheet. LMW CMC increased the breakage strain significantly with respect to the reference sheet at both relative humidities with all the dosages that were tested except with a 10 kg/t dosage at 50% RH. HMW CMC increased the breakage strain significantly only with dosages of 10, 20 and 50 kg/t and only at 80% RH. In this respect, LMW CMC turned out to have the greater potential of the two CMC polymers that were tested.

6. Conclusions

The primary objective of this thesis was to determine the effects of various polymeric additives on the physical properties of paper, especially the extensibility of paper in terms of the in-plane strain at the point of breakage. Cationic starch, GPAM and sequentially bi-layered GPAM + CMC showed the most significant improvements in terms of the tensile index, strength and breakage strain of a paper sheet. A polymer bi-layering technique using GPAM + CMC and CPAM + CMC combinations up to a dosage of 50 kg/t showed that there is a relatively good correlation between the breakage strain and tensile strength of paper hand sheets at 80% RH but this was not observed at 50% RH. This result indicated that the extensibility of paperboard can be increased by a higher tensile strength under selected conditions, as was also hypothesized.

It can be said that GPAM + CMC LMW (25% + 75%) showed best performance amongst the polymers that were tested considering the key properties as observed via dose- and type-specific responses. The differences between the different polymers or their combinations were insignificant at the 95% confidence level with almost every dosage.

It can be stated that by using high cationic strength additive dosage levels it seemed possible to control the paper formation by means of the application of high-shear (2000 rpm/90 sec) treatment prior to the sheet-forming step.

The tensile index, breakage strain and modulus of elasticity results of the sheets prepared with smaller (4.0 l) and larger (9.7 l) furnish volumes, implying a higher respective lower furnish consistency, using cationic starch indicated that a lower furnish volume and/or higher furnish consistency could have changed the fiber orientation significantly. This could provide higher breakage strains and lower moduli of elasticity, and yet at a maintained tensile index level. In order to validate the results in a scientifically sound way it would be necessary to repeat the tests using a higher number of parallel samples. It seems possible that a lower furnish volume and/or higher furnish consistency in forming might have been a better approach to adopt to get a greater difference in the breakage strain in between different test points.

The results of this thesis indicated that GPAM's ability to bond covalently with cellulose fibers can be one of the key properties that explain the improved strength and extensibility of paperboard. However, further experiments are needed to scientifically validate these indications.

GPAM and combined GPAM + CMC polymers showed potential for further development as extensibility additives for (thermo-) formable paperboard and as wet-strength additives for the improvement of the runnability of the wet paper web. By further developing and optimizing the properties of polymeric additives and other factors involved in papermaking it is possible to improve the extensibility of paperboard beyond the levels achieved with cationic starch. This would allow the replacement of non-renewable plastic packaging materials, e.g., for certain hot-pressing and deep-drawing applications.

References

1. [1] Britt K. W., Eastes J. W., American society for testing materials, presented at symposium on paper and paper products, Boston, Mass., 35, 1958
2. [2] Vishtal A., Tampere University of Technology, Formability of paper and its improvement, doctoral thesis, 2015
3. [3] Lindström T. et al., STFI-packforsk, On the nature of joint strength in paper - A review of dry and wet strength resins used in paper manufacturing, 2005
4. [4] Maloney T., Aalto University, Fibers and fiber products – course material, Fall 2015
5. [5] Mark R. E. et al., Published by Marcel Dekker, inc., Handbook of Physical Testing of Paper, vol. 1, New York, 2002
6. [6] Niskanen K., published by Fabet Oy, Papermaking Science and Technology, Paper Physics, Helsinki, 1998
7. [7] Zeng X. et al., "Elongination of paper", Bioresources 8(1), 472-486, 2013
8. [8] Seth R.S., Understanding sheet extensibility, Pulp & Paper Canada, 106(2), 33-40, 2005
9. [9] Ahlgren J. and Lundin T., Kemira Espoo R&D Center, Personal communication, 2015-2016
10. [10] Allan G. G. et al., Bonding in Paper and Nonwovens, Textile Research Journal, 42, 675-681, 1972
11. [11] Vishtal A. and Retulainen E., Boosting the Extensibility Potential of Fibre Networks: A review, BioResources, 9(4), 7933-7983, 2014
12. [12] Wågberg L., Ödberg L., Polymer adsorption on cellulosic fibres, Nordic Pulp Paper Res. J; 4(2), 135, 1989
13. [13] McQueen-Mason S. and Cosgrove D. J, Disruption of hydrogen bonding between plant cell wall polymers by proteins that induce wall extension, Proc. Nati. Acad. Sci. USA 91, 6574-6578, 1994
14. [14] Abdus S. et al., A New Class of Biobased Paper Dry Strength Agents: Synthesis and Characterization of Soy-Based Polymers, ACS Sustainable Chem. Eng. 3, 524-532, 2015

15. [15] Ahola S. et al., Cellulose nanofibrils—adsorption with poly(amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive, Cellulose, 15(2), 303-314, 2002
16. [16] Gustafsson E., Tailoring adhesion and wetting properties of cellulose fibers and model surfaces, Licentiate thesis, KTH Royal Institute of Technology, Stockholm, 2012
17. [17] Svensson A. et al., 3D-shapeable thermoplastic paper materials, Nordic Pulp & Paper Research Journal, 28(4), 2013
18. [18] Teeri T. et al., Biomimetic engineering of cellulose-based materials, TRENDS in Biotechnology Vol. 25 No. 7, 2007
19. [19] Hubbe M. A., Bonding between fibers in the absence and presence of dry-strength agents – a review, BioResources 1(2), 281-318, 2006
20. [20] Larsson P. A. et al., Highly ductile fibres and sheets by core-shell structuring of the cellulose nanofibrils, Cellulose 21(1), 323-333, 2014
21. [21] Myllytie P., Helsinki university of technology, Interactions of polymers with fibrillar structure of cellulose fibres: A new approach to bonding and strength in paper, Doctoral Thesis, 2009
22. [22] Espy H. H., The mechanism of wet-strength development in paper: a review, Tappi Journal, 78(4), 1995
23. [23] Reynolds W. F. et al., Published by Technical Association of the Pulp and Paper Industry, Inc., Dry strength additives, Tappi Press, USA, 1980
24. [24] Levlin J. and Söderhjelm L., KCL, The Finnish Pulp and Paper Research Institute , Papermaking science and technology, Pulp and Paper Testing, 1999
25. [25] Biermann C. J., Published by Academic Press Limited, Handbook of pulping and papermaking, second edition, London, 1996
26. [26] Reinhardt H. W., "On the biaxial testing and strength of coated fabrics", Experimental Mechanics, 16(2), 71-74, 1976
27. [27] Tryding J., Lund university, Research project report, In-plane fracture of paper, Sweden, 1996
28. [28] Mäkelä P., presented at 14th Fundamental Research Symposium: Advances in Pulp and Paper Science Research, Effect of drying conditions on the tensile properties of paper, Oxford, 2009

29. [29] Seth R. S. and Page D. H., “The stress strain curve of paper”, in The Role of Fundamental Research in Paper Making, Transactions of the Symposium Held at Cambridge: September 1981, Volume 1, 421-452. Ed. Brander J. Mechanical Engineering Publications Limited, London, 1983
30. [30] Stenius P., published by Fapet Oy, Papermaking science and technology, Forest Products Chemistry, Helsinki, 2000
31. [31] Badel E., Acclimation of mechanical and hydraulic functions in trees: impact of the thigmomorphogenetic process, Front. Plant Sci., 6, 266, 2015
32. [32] Page, D. H. and El-Hosseiny, F., The mechanical properties of single wood pulp fibers. Part VI. Fibril angle and the shape of the stress-strain curve. Pulp Pap. Can. 84(9), TR 99-100, 1983
33. [33] Page D. H. and Seth R. S., The elastic modulus of paper III. The effect of dislocations, microcompressions, curl, crimps and kinks. Tappi J. 6310, 99-101, 1980
34. [34] Wathen R., Helsinki University of Technology, Studies on fiber strength and its effect on paper properties, Doctoral thesis, Helsinki, 2006
35. [35] Forsström, J. et al., Influence of fibre/fibre joint strength and fibre flexibility on the strength of papers from unbleached kraft fibers. Nord. Pulp Pap. Res. J. 20(2) 186-191, 2005
36. [36] Paulapuro H., published by Fapet Oy, Papermaking science and technology, Papermaking part 1, Stock preparation and wet end, Helsinki, 2007
37. [37] Marais A. et al., New insights into the mechanisms behind the strengthening of lignocellulosic fibrous networks with polyamines, Cellulose, 21, 3941-3950, 2014
38. [38] Alince B., Cationic latex as a multifunctional papermaking wet-end additive, Tappi Journal, 82(3), 175-187, 1999
39. [39] Kallmes O. et al., The structure of paper II, The statistical geometry of a multiplanar fiber network, Tappi, 44(7), 519, 1961
40. [40] Dent R. W., Inter-fiber Distances in Paper and Nonwovens, The Journal of The Textile Institute, 92(1), 63-74, 2001
41. [41] Neimo L., published by Fapet Oy, Papermaking science and technology, Papermaking chemistry, Helsinki, 1999
42. [42] Holik H., published by Wiley-VCH, Handbook of paper and board, 2006

43. [43] Davison R.W., Weak link in paper dry strength, Tappi, 55, 567-573, 1972
44. [44] Whistler L. R. et al., published by Academic Press, Starch, Chemistry and Technology, second edition, USA, 1984
45. [45] Pal S. et al., Cationic starch: an effective flocculating agent, Carbohydrate Polymers, 59, 417-423, 2005
46. [46] Dumitriu, S., published by Marcel Dekker, Inc., Polysaccharides: Structural Diversity and Functional Versatility, Second Edition, New York, 2005
47. [47] Vert M., Terminology for biorelated polymers and applications (IUPAC Recommendations 2012), Pure Appl. Chem., 84(2), 377-410, 2012
48. [48] Grigoriev V. et al., Technical paper, Kemira oyj, Strength chemistry for board and tissue production: Scientific outlook and end applications, Presented at PAP-FOR, St. Petersburg, Russia, 2012
49. [49] Mathur N. K., published by CRC Press, Industrial Galactomannan Polysaccharides, London and New York, 2012
50. [50] Scheller H. V., Ulvskov P., Hemicelluloses, Annu. Rev. Plant Biol. 61, 263-89, 2010
51. [51] Laine J., Fiber surface modification by different polyelectrolytes – possibility to obtain new paper properties, PulPaper 2007 Conference, Helsinki, 2007
52. [52] Wilson A. D. and Prosser H. J., published by Elsevier, Developments in ionic polymers – 2, London and New York, 1986
53. [53] Chan L. L., published by TAPPI Press, Wet-strength resins and their applications, 1994
54. [54] Nechyporchuk O. et al., Production of cellulose nanofibrils: A review of recent advances, Industrial Crops and Products, 93(2), 25, 2016
55. [55] NPL Manual, Manual for the Calculation of Elastic-Plastic Materials Models Parameters, Queen's Printer, UK, 2007
56. [56] Vishtal A. and Retulainen E., Deep-drawing of paper and paperboard: The role of material properties, Bioresources 7(3), 4424-4450, 2012
57. [57] Borodulina S. et al., Stress-strain curve of paper revisited, Nordic Pulp and Paper Research Journal, 27(2), 2012

58. [58] Eriksson M. et al., “Application of polymeric multilayers of starch onto wood fibres to enhance strength properties of paper”, Nordic Pulp Paper Res. J., 20(3), 270, 2005a
59. [59] Eriksson M. et al., “The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibres”, J. Colloid Interface Sci., 2005b
60. [60] Pelton R. H., “On the Design of Polymers for Increased Paper Dry Strength – a Review”, Appita Journal, 57(3), 181-190, 2004
61. [61] Alava, M., Niskanen, K., “The physics of paper,” Rep. Prog. Phys. 69, 669-723, 2006
62. [62] Mäkelä P., Östlund S., Orthotropic elastic-plastic material model for paper materials, International Journal of Solids and Structures, 40, 5599-5620, 2003
63. [63] Xia, Q.S. et al, A constitutive model for the anisotropic elastic–plastic deformation of paper and paperboard. International Journal of Solids and Structures 39 (15), 4053-4071, 2002
64. [64] Vainio A., Aalto university, Interfibre bonding and fiber segment activation in paper – observations on the phenomena and their influence on paper strength properties, doctoral thesis , 2007
65. [65] Wågberg L., Mid Sweden University, Polyelectrolyte adsorption on cellulose fibres – a review, Report number: R-00-7, 2001
66. [66] Ford N. et al, Int. J. Innov. Mgt. 18(05), 1450033, 2014
67. [67] Tanninen P. et al., The effect of tool heating arrangement on fibre material forming. Journal of Materials Processing Technology 214, 1576-1582, 2014a
68. [68] Tanninen, P. et al., Thermal and mechanical durability of starch-based dual polymer coatings in the press forming of paperboard, Packag. Technol. Sci. 27, 353-363, 2014b
69. [69] Leminen, V. et al., Combined effect of paperboard thickness and mould clearance in the press forming process. Bioresources 8(4), 5701-5714, 2013
70. [70] Kunnari V. et al., Formable paper for new packaging applications, presented at 23rd Symp. International Association of Packaging Research Institutes (IAPRI), UK, 2007

71. [71] Linvill E. and Östlund, S. The combined effects of moisture and temperature on the mechanical response of paper. Experimental Mechanics 54(8), 1329-1341, 2014
72. [72] Altaner C. M. et al., How cellulose stretches: Synergism between covalent and hydrogen bonding. Biomacromolecules 15(3), 791-798, 2014
73. [73] Hagiopol C. and Johnston J. W., Published by CRC Press, "Chemistry of modern papermaking", London and New York, 2012
74. [74] Spence G. G., published by TAPPI Press, Wet- and dry-strength additives – application, retention and performance, Atlanta, 1999
75. [75] Wågberg, L., On the mechanism behind the action of dry and wet strength agents, 5th International Paper and Coating Symposium, Montreal, 281, 2003
76. [76] Feg X. and Pelton R., Polyvinylamine CMC complexes, presented at 5th International Paper and Coating Symposium, Montreal, 361, 2003
77. [77] Chew Y. et al., Characterization of the stability of cationic starch stabilised AKD emulsions, presented at 5th International Paper and Coating Symposium, Montreal, 331, 2003
78. [78] Laleg M., Pikilik I., Strengthening of mechanical pulp webs by chitosan, Nordic Pulp and Paper Res. J., 7 (4), 174, 1992
79. [79] Tanninen P., Lappeenranta university of technology, Press forming of paperboard – advancement of converting tools and process control, doctoral thesis, 2015
80. [80] Leminen V., Lappeenranta university of technology, Leak-proof heat sealing of press-formed paperboard trays, doctoral thesis, 2016
81. [81] Östlund M. et al., Influence of paperboard structure and processing conditions on forming of complex paperboard structures, Packaging Technology and Science, 24(6), 331-341, 2011
82. [82] Andersson C., New ways to enhance the functionality of paperboard by surface treatment – a review. Packaging Technology and Science, 21(6), 339-373, 2008
83. [83] Hauptmann M. and Majschak, J., New quality level of packaging components from paperboard through technology improvement in 3D forming, Packaging Technology and Science 24(7), 419-432, 2011
84. [84] Website http://reid.wrap.org.uk/item.php?id=46 (Accessed 9th of august 2016)

85. [85] Niskanen K. (Ed.), published by Walter de Gruyter, Mechanics of Paper Products, p. 13, Berlin and Boston, 2012
86. [86] Tillman O., published by John Wiley & Sons., Ullmann's Encyclopedia of Industrial Chemistry, Paper and Board, 11. Grades and Their Properties, 2, New York, 2012
87. [87] Marais A. et al., Towards a superstrainable paper using the layer-by-layer technique, Carbohydrate Polymers 100(1), 218-224, 2014
88. [88] Rangachari K. and Kays Chinai K., Patent US 6310268 B1, Non-ionic plasticizer additives for wood pulps and absorbent cores, 2001
89. [89] Petterson G. et al., Increased joint-forming ability of ductile kraft pulp fibres by polyelectrolyte multilayer treatment – Influence of refining and drying strategies, Nordic Pulp and Paper Research Journal, 22(2), 228-235, 2007
90. [90] Janssen L. P. B. M. and Moscicki L., Thermoplastic starch as packaging material, Acta Sci. Pol., Technica Agraria 5(1), 19-25, 2006
91. [91] de Graaf R. A. et al., Material properties and glass transition temperatures of differential thermoplastic starches after extrusion processing. Starch. 55, 80-86, 2003
92. [92] Borgqvist E. et al., Distortional hardening plasticity model for paperboard, International Journal of Solids and Structures, 51(13), 2411-2423, 2014
93. [93] Ramasubramanian, M. K. and Wang, Y. Y., Constitutive models for paper and other ribbon-like nonwovens—a literature review. In: Perkins, R. (Ed.), Mechanics of Cellulosic Materials, published by The American Society of Mechanical Engineers, New York, 31-42, 1999
94. [94] Mäkelä P. and Östlund S., Orthotropic elastic-plastic material model for paper materials, International Journal of Solids and Structures 40, 5599-5620, 2003
95. [95] Mendelson, A. and Plasticity: Theory and Application, published by Macmillan, New York, 1968
96. [96] Haslach H. W. Jr., The Moisture and Rate-Dependent Mechanical Properties of Paper: A Review, Mechanics of Time-Dependent Materials 4, 169-210, 2000
97. [97] Haslach H. W. Jr., A model for drying-induced microcompressions in paper: Buckling in the inter-fiber bonds, Composites Part B: Engineering, 27(1), 25-33, 1996

98. [98] Alén, R, Structure and chemical composition of wood, In: Forest Products Chemistry, P. Stenius, (Ed.), published by Fapet Oy, Helsinki, 11-57, 2000
99. [99] Hirn U. and Schennach R., Comprehensive analysis of individual pulp fiber bonds quantifies the mechanisms of fiber bonding in paper, Scientific Reports 5, Article number: 10503, 2015
100. [100] ISO standards handbook; Paper, board and pulps Vol. 1, Third edition, 2003
101. [101] ISO standards handbook; Paper, board and pulps Vol. 2, Third edition, 2003
102. [102] Kemira Oyj instruction, version 2.0, Paperin ja kartongin vetolujuuden määrittäminen, EIMS-68-28, 2016
103. [103] Kemira instruction; Viskositeetti-3-Vsa-18, Viskositeetin mittaus brookfield –viskosimetrillä –yleisohje, EIMS-5-24, version 5-0, 2015
104. [104] Roy D. et al., Cellulose modification by polymer grafting: a review, Chem. Soc. Rev., 38, 2046-2064, 2009
105. [105] Rojas O. J. and Neuman R. D., Adsorption of polysaccharide wet-end additives in papermaking systems, Colloids and Surfaces A: Physicochem. Eng. Aspects 155, 419-432, 1999
106. [106] Hubbe M. A., Reversibility of polymer-induced fiber flocculation by shear. 1. Experimental methods. Nord. Pulp Paper Res. J. 15(5), 545-553, 2000
107. [107] Hubbe M. A. et al., "Retention aids interaction, review", Bioresources, 4(2), 850-906, 2009

Date	Test number	Stock preparation						Hand sheet preparation		
		SR°	pH		Cond.	Additive/polymer		dewatering time (avg. of three measurements)	Furnish volume	amount of 0.4 % pulp /hand sheet
			initial	adj.		quality	dosage			
					[mS/cm]		[kg/dry t]	[sec ± 1]	[l]	[g]
6.4.2016	1	29	6.9	-	-	no polymer	0	5	4.0	784
6.4.2016	2	29	6.9	-	-	Cationic starch (0.08%/4.0L furnish)	20	5	4.0	831
7.4.2016	3	29	6.9	-	-		50	6	4.0	839
7.4.2016	4	29	6.9	-	-		100	7	4.0	830
8.4.2016	5	29	7.2	-	-		200	10	4.0	832
8.4.2016	6	29	7.2	-	-		400	15	4.0	804
12.4.2016	7	28	7.6	6.9	0.7	no polymer	0	11	9.7	860
12.4.2016	8	28	7.6	6.9	0.7	Cationic starch (0.03%/9.7L furnish)	5	11	9.7	860
13.4.2016	9	28	7.7	6.9	0.7		10	11	9.7	849
13.4.2016	10	28	7.7	7.0	0.7		20	12	9.7	845
14.4.2016	11	28	7.7	7.1	0.9		50	14	9.7	858
14.4.2016	12	28	7.7	7.1	0.7	PAAE high ECH	5	10	9.7	850
15.4.2016	13	28	7.7	7.0	0.7		10	11	9.7	842
18.4.2016	14	27	7.6	-	0.7	no polymer	0	10	9.7	855
18.4.2016	15	27	7.6	-	0.7	PAAE high ECH	20	11	9.7	852
19.4.2016	16	27	7.6	-	0.7		50	11	9.7	838
19.4.2016	17	27	7.6	-	0.7	PAAE high ECH + CMC HMW (40% + 60%)	5	13	9.7	844
20.4.2016	18	27	7.6	-	0.7		10	13	9.7	840
20.4.2016	19	27	7.6	-	0.7		20	14	9.7	830
21.4.2016	20	27	7.5	-	0.7		50	20	9.7	815
21.4.2016	21	27	7.5	-	0.7	Chitosan LMW in 0.24% adipic acid	5	11	9.7	815
22.4.2016	22	27	7.5	-	0.7		10	11	9.7	812
22.4.2016	23	27	7.5	-	0.7		20	11	9.7	789
25.4.2016	24	25	7.6	-	0.7	no polymer	0	10	9.7	805
25.4.2016	25	25	7.6	-	0.7	Chitosan LMW in 0.24%	50	11	9.7	777
26.4.2016	26	25	7.6	-	0.7	Chitosan HMW in 0.24% adipic acid	5	10	9.7	811
26.4.2016	27	25	7.6	-	0.7		10	10	9.7	784
27.4.2016	28	25	7.6	-	0.7		20	10	9.7	776
27.4.2016	29	25	7.6	-	0.7		50	11	9.7	781
29.4.2016	30	25	7.6	-	0.7	Chitosan HMW in 2% citric acid	5	9	9.7	803
29.4.2016	31	25	7.6	-	0.7		10	9	9.7	784
2.5.2016	32	25	7.6	-	0.7	no polymer	0	9	9.7	860
2.5.2016	33	25	7.6	-	0.7	Chitosan HMW in 2% citric acid	20	10	9.7	840
3.5.2016	34	25	7.5	-	0.7		50	10	9.7	858
3.5.2016	35	25	7.5	-	0.7	Cationic NFC	5	9	9.7	830
4.5.2016	36	25	7.6	-	0.7		10	10	9.7	856
4.5.2016	37	25	7.6	-	0.7		20	10	9.7	831
6.5.2016	38	25	7.7	-	0.7		50	11	9.7	848
6.5.2016	39	25	7.7	-	0.7	Cationic NFC+PLA (50% + 50%)	5	9	9.7	830

Date	Test number	Stock preparation						Hand sheet preparation		
		SR°	Ph		Cond.	Additive/polymer		dewatering time (avg. of three measurements)	Furnish volume	amount of 0.4 % pulp /hand sheet
			initial	adj.		quality	dosage			
					[mS/cm]		[kg/dry t]	[sec ± 1]	[l]	[g]
9.5.2016	40	26	7.6	-	0.7	no polymer	0	9	9.7	685
10.5.2016	41	26	7.7	-	0.7	Cationic NFC + PLA (50% + 50%)	10	9	9.7	725
10.5.2016	42	26	7.7	-	0.7		20	10	9.7	718
11.5.2016	43	26	7.7	-	0.7		50	12	9.7	797
11.5.2016	44	26	7.7	-	0.7		50	12	9.7	792
12.5.2016	45	26	7.7	-	0.7	GPAM	5	9	9.7	832
12.5.2016	46	26	7.7	-	0.7		10	10	9.7	815
13.5.2016	47	26	7.6	-	0.7		20	10	9.7	841
16.5.2016	48	26	7.7	-	0.7	no polymer	0	8	9.7	803
16.5.2016	49	26	7.7	-	0.7	GPAM	50	11	9.7	781
17.5.2016	50	26	7.6	-	0.7	CPAM 2 (10 mol-% / SV0.5% 72 mPas)	5	9	9.7	823
17.5.2016	51	26	7.6	-	0.7		10	9	9.7	793
18.5.2016	52	26	7.6	-	0.7		20	10	9.7	826
18.5.2016	53	26	7.6	-	0.7		50	10	9.7	785
19.5.2016	54	26	7.6	-	0.7	CPAM 3 (6 mol-% / SV 3.4 mPas)	5	11	9.7	807
19.5.2016	55	26	7.6	-	0.7		10	14	9.7	803
20.5.2016	56	26	7.7	-	0.7		20	21	9.7	822
20.5.2016	57	26	7.7	-	0.7		50	37	9.7	804
23.5.2016	58	27	7.6	-	0.7	no polymer	0	9	9.7	790
23.5.2016	59	27	7.6	-	0.7	CPAM 4 (2 mol-% / SV 3.4 mPas)	5	9	9.7	754
24.5.2016	60	27	7.6	-	0.7		10	11	9.7	782
24.5.2016	61	27	7.6	-	0.7		20	14	9.7	773
25.5.2016	62	27	7.6	-	0.7		50	24	9.7	764
25.5.2016	63	27	7.6	-	0.7	Cationic guar gum	5	9	9.7	764
26.5.2016	64	27	7.6	-	0.7		10	10	9.7	795
26.5.2016	65	27	7.6	-	0.7		20	12	9.7	789
27.5.2016	66	27	7.6	-	0.7		50	15	9.7	796
27.5.2016	67	27	7.6	-	0.7	PAAE low ECH	5	9	9.7	773
30.5.2016	68	27	7.7	-	0.7	no polymer	0	9	9.7	772
30.5.2016	69	27	7.7	-	0.7	PAAE low ECH	10	9	9.7	758
31.5.2016	70	27	7.7	-	0.7		20	9	9.7	763
31.5.2016	71	27	7.7	-	0.7		50	9	9.7	743

Date	Test number	Stock preparation						Hand sheet preparation		
		SR°	Ph		Cond.	Additive/polymer		dewatering time (avg. of three measurements)	Furnish volume	amount of 0.4 % pulp /hand sheet
			initial	adj.		quality	dosage			
					[mS/cm]		[kg/dry t]	[sec ± 1]	[l]	[g]
1.6.2016	72	27	7.7	-	0.7	CPAM 1 (10 mol-% / SV0.5% 10 mPas)	5	8	9.7	757
1.6.2016	73	27	7.7	-	0.7		10	8	9.7	747
2.6.2016	74	27	7.7	-	0.7		20	9	9.7	775
3.6.2016	75	27	7.7	-	0.7		50	9	9.7	768
3.6.2016	76	27	7.7	-	0.7	GPAM	100	9	9.7	750
6.6.2016	77	28	7.7	-	0.7	no polymer	0	8	9.7	690
6.6.2016	78	28	7.7	-	0.7	GPAM + CMC HMW (50% + 50%)	5	9	9.7	683
7.6.2016	79	28	7.7	-	0.7		10	9	9.7	699
7.6.2016	80	28	7.7	-	0.7		20	9	9.7	696
8.6.2016	81	28	7.7	-	0.7		50	8	9.7	690
8.6.2016	82	28	7.7	-	0.7		100	8	9.7	676
9.6.2016	83	28	7.6	-	0.7	PAH + HA (20% + 80%)	5	8	9.7	704
9.6.2016	84	28	7.6	-	0.7		10	9	9.7	690
10.6.2016	85	28	7.6	-	0.7		20	9	9.7	702
14.6.2016	86	26	7.7	-	0.7	no polymer	0	8	9.7	833
14.6.2016	87	26	7.7	-	0.7	PAH + HA (20% + 80%)	50	9	9.7	792
16.6.2016	89	26	7.5	-	0.7	Chitosan HMW in 0.24% adipic acid	20	10	9.7	800
15.6.2016	88	26	7.5	-	0.7	no polymer	0	8	9.7	826
16.6.2016	90	26	7.5	-	0.7	Cationic starch	50	10	9.7	806
17.6.2016	91	26	7.5	-	0.7	GPAM	50	11	9.7	832
17.6.2016	92	26	7.5	-	0.7	GPAM + CMC HMW (50% + 50%)	50	8	9.7	796
5.7.2016	93	27	7.8	-	0.7	no polymer	0	9	9.7	810
5.7.2016	94	27	7.8	-	0.7	GPAM + CMC HMW (25% + 75%)	5	10	9.7	808
5.7.2016	95	27	7.8	-	0.7		10	10	9.7	800
6.7.2016	96	27	7.7	-	0.7		20	11	9.7	822
6.7.2016	97	27	7.7	-	0.7		50	11	9.7	817
7.7.2016	98	27	7.7	-	0.7	GPAM + CMC HMW (75% + 25%)	5	9	9.7	803
7.7.2016	99	27	7.7	-	0.7		10	8	9.7	806
7.7.2016	100	27	7.7	-	0.7		20	7	9.7	794
8.7.2016	101	27	7.7	-	0.7		50	6	9.7	793
11.7.2016	102	27	7.8	-	0.7	no polymer	0	8	9.7	790
11.7.2016	103	27	7.8	-	0.7	GPAM + CMC LMW (25% + 75%)	5	8	9.7	787
12.7.2016	104	27	7.7	-	0.7		10	9	9.7	798
12.7.2016	105	27	7.7	-	0.7		20	9	9.7	787
13.7.2016	106	27	7.7	-	0.7		50	10	9.7	800
13.7.2016	107	27	7.7	-	0.7	CPAM 2 + CMC LMW (25% + 75%)	5	8	9.7	789
14.7.2016	108	27	7.7	-	0.7		10	8	9.7	787
14.7.2016	109	27	7.7	-	0.7		20	9	9.7	798
14.7.2016	110	27	7.7	-	0.7		50	9	9.7	782

Appendix 4/7

Test	Additive/polymer		Measurements from handsheets (average of eight sheets)																																	
			Grammage		Tensile strength										Modulus of elasticity				Density				Breakage strain								Thickness		Beta formation			
	quality	dosage	(RH 50 %)		Tensile strength		Tensile index		Norm. tensile index		Tensile strength		Norm. tensile strength		RH 50%				RH 50%				RH 50 %				RH 80 %				RH 50 %		RH 50%			
					RH 50%		RH 50%		RH 50%		RH 80%		RH 80%		measured		normalized		measured		normalized		measured		normalized		measured		normalized				measured		normalized	
		[kg/dry t]	[g/m²]	S.D.	[kN/m]	S.D.	[Nm/g]	S.D.	TI/TI$_{ref}$	S.D.	[kN/m]	S.D.	TS/TS$_{ref}$	S.D.	[Gpa]	S.D.		S.D.	[g/cm³]	S.D.		S.D.	[%]	S.D.	BS/BS$_{ref}$	S.D.	[%]	S.D.	BS/BS$_{ref}$	S.D.	[µm]	S.D.		2*S.D.		S.D.
1	no polymer	0	119.3	1.6	7.8	0.43	65.6	3.60	1.00	0.00	6.3	0.60	1.00	0.00	4.5	0.1	1.00	0.00	0.66	0.02	1.00	0.00	3.6	0.3	1.00	0.00	4.0	0.3	1.00	0.00	181	8	7.7	0.4	1.0	0.0
2	Cationic starch (0.08%/4.0L furnish)	20	126.2	1.3	10.4	0.72	82.4	5.67	1.26	0.09	8.4	0.56	1.32	0.09	5.2	0.2	1.15	0.04	0.69	0.01	1.04	0.02	3.7	0.3	1.03	0.07	4.3	0.1	1.10	0.03	183	4	6.2	0.3	0.7	0.1
3		50	128.0	1.8	10.9	0.67	85.4	5.27	1.30	0.07	8.9	0.59	1.41	0.09	5.3	0.2	1.00	0.04	0.71	0.02	1.07	0.02	3.7	0.3	1.04	0.08	4.3	0.3	1.09	0.07	181	5	6.7	0.5	1.0	0.1
4		100	127.9	1.3	11.2	0.74	87.4	5.80	1.31	0.07	9.3	0.46	1.47	0.07	5.2	0.2	0.98	0.04	0.72	0.02	1.09	0.03	4.0	0.2	1.11	0.04	4.6	0.2	1.17	0.06	178	5	6.1	0.3	0.9	0.0
5		200	127.1	1.4	11.2	0.78	88.4	6.10	1.35	0.09	-	-	-	-	5.4	0.3	1.01	0.06	0.71	0.01	1.07	0.02	3.8	0.2	1.06	0.06	-	-	-	-	181	4	6.6	0.4	0.9	0.1
6		400			-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
7	no polymer	0	131.5	1.8	8.9	0.70	67.7	5.35	1.00	0.00	7.3	0.32	1.00	0.00	4.4	0.2	1.00	0.00	0.67	0.03	1.00	0.00	4.0	0.3	1.00	0.00	4.3	0.3	1.00	0.00	194	8	6.8	0.7	1.0	0.0
8	Cationic starch (0.03%/9.7L furnish)	5	128.7	1.7	10.1	0.59	78.1	4.81	1.15	0.07	8.1	0.20	1.11	0.03	4.8	0.2	1.09	0.04	0.68	0.01	1.01	0.02	3.9	0.3	0.99	0.07	4.4	0.2	1.00	0.05	190	5	6.7	0.5	1.0	0.1
9		10	129.7	2.3	10.2	0.43	77.2	3.33	1.15	0.05	8.3	0.31	1.14	0.04	4.8	0.2	1.09	0.03	0.69	0.01	1.02	0.02	3.8	0.2	0.97	0.05	4.4	0.3	1.02	0.08	190	5	7.1	0.8	1.0	0.1
10		20	129.2	1.7	11.4	0.88	87.9	6.79	1.30	0.10	9.2	0.41	1.26	0.06	5.2	0.2	1.18	0.04	0.70	0.01	1.04	0.02	4.0	0.4	1.00	0.10	4.3	0.3	0.99	0.06	186	9	5.3	0.4	0.8	0.1
11		50	130.4	2.0	11.6	0.24	89.2	1.87	1.32	0.03	9.9	0.35	1.36	0.05	5.1	0.1	1.16	0.03	0.69	0.01	1.02	0.02	3.9	0.2	0.98	0.04	4.5	0.1	1.04	0.02	190	4	5.0	0.2	0.7	0.0
12	PAAE high ECH	5	127.1	1.9	9.6	0.45	75.4	3.57	1.11	0.05	7.9	0.40	1.09	0.06	4.7	0.2	1.07	0.05	0.67	0.01	1.00	0.02	3.7	0.2	0.94	0.05	4.2	0.3	0.97	0.06	189	4	6.3	0.4	0.9	0.1
13		10	127.5	1.9	10.4	0.50	81.9	3.92	1.21	0.05	8.9	0.37	1.21	0.05	4.9	0.3	1.12	0.06	0.67	0.02	0.99	0.03	3.8	0.2	0.96	0.06	4.5	0.2	1.03	0.04	190	7	5.2	0.1	0.8	0.0
14	no polymer	0	129.5	1.3	8.8	0.41	68.0	3.18	1.00	0.00	7.3	0.36	1.00	0.00	4.2	0.2	1.00	0.00	0.66	0.01	1.00	0.00	4.0	0.3	1.00	0.00	4.5	0.2	1.00	0.00	199	5	6.8	0.4	1.0	0.0
15	PAAE high ECH	20	130.7	1.4	10.0	0.30	76.2	2.26	1.12	0.04	8.5	0.47	1.15	0.06	4.7	0.1	1.13	0.02	0.69	0.01	1.05	0.02	3.9	0.2	0.97	0.04	4.6	0.3	1.00	0.06	190	4	5.5	0.2	0.8	0.0
16		50	128.6	1.1	9.9	0.55	77.1	4.25	1.13	0.05	8.3	0.55	1.15	0.08	4.5	0.1	1.08	0.03	0.66	0.01	1.01	0.01	4.0	0.2	0.99	0.06	4.5	0.1	1.00	0.03	193	3	5.5	0.2	0.8	0.0
17	PAAE high ECH + CMC HMW (40% + 60%)	5	133.3	1.3	9.9	0.73	74.4	5.44	1.09	0.08	8.3	0.56	1.11	0.08	4.7	0.1	1.12	0.02	0.67	0.01	1.03	0.02	3.8	0.4	0.95	0.11	4.4	0.3	0.97	0.06	198	5	6.3	0.2	0.9	0.0
18		10	127.1	1.4	10.4	0.72	82.1	5.68	1.21	0.08	9.3	0.31	1.30	0.04	5.0	0.1	1.20	0.02	0.70	0.02	1.06	0.02	3.8	0.4	0.93	0.09	4.7	0.3	1.04	0.06	183	5	6.0	0.4	0.9	0.1
19		20	127.9	1.6	10.6	0.75	82.5	5.89	1.21	0.09	9.3	0.54	1.29	0.07	5.1	0.2	1.21	0.03	0.71	0.02	1.08	0.03	3.9	0.3	0.97	0.08	4.6	0.3	1.01	0.07	181	5	6.5	0.6	0.9	0.1
20		50	128.1	1.0	11.0	0.50	86.0	4.20	1.27	0.06	9.8	0.72	1.36	0.11	5.1	0.1	1.21	0.01	0.71	0.02	0.98	0.34	4.0	0.2	0.99	0.06	4.7	0.3	1.04	0.07	180	6	5.9	0.5	0.8	0.1
21	Chitosan LMW in 0.24% adipic acid	5	129.2	1.0	9.4	0.63	72.7	4.91	1.06	0.07	8.1	0.33	1.11	0.04	4.8	0.1	1.14	0.02	0.69	0.02	1.06	0.03	3.8	0.3	0.94	0.07	4.4	0.2	0.98	0.03	186	6	6.3	0.7	0.9	0.0
22		10	131.5	0.7	9.4	0.41	71.8	3.15	1.06	0.04	8.3	0.60	1.14	0.08	4.9	0.2	1.16	0.04	0.68	0.01	1.03	0.02	3.5	0.2	0.87	0.04	4.3	0.3	0.94	0.06	195	4	6.1	0.2	0.9	0.0
23		20	129.4	1.1	9.4	0.40	72.4	3.10	1.06	0.04	8.6	0.58	1.18	0.08	4.9	0.1	1.16	0.03	0.67	0.02	1.03	0.03	3.7	0.1	0.91	0.03	4.5	0.3	0.98	0.06	192	7	6.6	0.1	1.0	0.0
24	no polymer	0	131.4	0.6	9.3	0.33	70.5	2.53	1.00	0.00	7.4	0.29	1.00	0.00	4.7	0.2	1.00	0.00	0.69	0.02	1.00	0.00	4.1	0.2	1.00	0.00	4.4	0.3	1.00	0.00	186	20	6.3	0.3	1.0	0.0
25	Chitosan LMW in 0.24%	50	130.9	1.6	9.2	0.23	69.9	1.78	0.99	0.03	8.0	0.66	1.08	0.09	4.8	0.2	1.03	0.04	0.70	0.02	1.02	0.02	3.7	0.3	0.92	0.06	4.4	0.4	1.00	0.10	186	5	6.6	0.4	1.1	0.1
26	Chitosan HMW in 0.24% adipic acid	5	131.5	1.3	9.5	0.49	72.4	3.75	1.03	0.06	8.1	0.33	1.08	0.04	4.8	0.2	1.00	0.03	0.67	0.01	0.97	0.01	3.8	0.2	0.93	0.04	4.5	0.3	1.01	0.06	196	5	6.1	0.3	1.0	0.1
27		10	131.3	1.0	9.0	0.38	68.6	2.89	0.97	0.04	7.6	0.29	1.02	0.04	4.5	0.1	0.98	0.03	0.68	0.01	0.99	0.01	3.8	0.3	0.94	0.06	4.5	0.2	1.01	0.05	192	3	7.7	0.3	1.2	0.1
28		20	128.2	1.4	8.0	0.62	62.2	4.80	0.88	0.06	6.9	0.46	0.93	0.06	4.2	0.3	0.89	0.05	0.64	0.03	0.93	0.04	3.6	0.2	0.87	0.05	4.2	0.3	0.97	0.06	200	10	9.6	0.5	1.5	0.1
29		50	129.8	1.0	8.8	0.47	68.0	3.65	0.96	0.05	7.5	0.58	1.00	0.08	4.5	0.1	0.96	0.03	0.67	0.03	0.96	0.04	3.8	0.2	0.93	0.04	4.3	0.3	0.98	0.08	195	8	7.6	0.6	1.2	0.1
30	Chitosan HMW in 2% citric acid	5	128.8	1.4	9.1	0.75	71.0	5.79	1.01	0.08	7.2	0.45	0.97	0.06	4.4	0.1	0.95	0.02	0.64	0.01	0.93	0.02	3.9	0.4	0.96	0.07	4.4	0.3	1.01	0.07	202	6	6.7	0.3	1.1	0.1
31		10	127.6	0.8	9.3	0.22	73.2	1.70	1.04	0.03	7.3	0.43	0.98	0.06	4.4	0.2	0.93	0.03	0.63	0.02	0.91	0.02	4.1	0.2	1.00	0.06	4.4	0.3	1.01	0.08	202	5	6.5	0.4	1.0	0.1

Appendix 5/7

Test	Additive/polymer		Measurements from handsheets (average of eight sheets)																															
			Grammage		Tensile strength										Modulus of elasticity				Density				Breakage strain								Thickness		Beta formation			
	quality	dosage	(RH 50 %)		Tensile strength		Tensile index		Norm. tensile index		Tensile strength		Norm. tensile strength		RH 50%				RH 50%				RH 50 %				RH 80 %				RH 50 %		RH 50%			
					RH 50%		RH 50%		RH 50%		RH 80%		RH 80%		measured		normalized		measured		normalized		measured		normalized		measured		normalized						
		[kg/dry t]	[g/m^2]	S.D.	[kN/m]	S.D.	[Nm/g]	S.D.	TI/TI$_{ref}$	S.D.	[kN/m]	S.D.	TS/TS$_{ref}$	S.D.	[Gpa]	S.D.		S.D.	[g/cm^3]	S.D.		S.D.	[%]	S.D.	BS/BS$_{ref}$	S.D.	[%]	S.D.	BS/BS$_{ref}$	S.D.	[µm]	S.D.		2*S.D.		S.D.
32	no polymer	0	131.0	1.1	9.7	0.31	74.2	2.35	1.00	0.00	7.7	0.54	1.00	0.00	4.4	0.2	1.00	0.00	0.66	0.02	1.00	0.00	4.2	0.3	1.00	0.00	4.5	0.3	1.00	0.00	199	6	6.0	0.2	1.0	0.0
33	Chitosan HMW in 2% citric acid	20	129.3	0.5	10.0	0.59	77.6	4.55	1.05	0.06	8.0	0.38	1.03	0.05	4.8	0.1	1.08	0.03	0.66	0.01	1.00	0.02	3.9	0.4	0.94	0.08	4.4	0.3	0.97	0.06	196	4	5.7	0.2	0.9	0.0
34		50	130.0	1.5	10.1	0.24	77.5	1.82	1.05	0.03	7.8	0.68	1.01	0.09	4.9	0.1	1.10	0.01	0.67	0.01	1.01	0.02	4.0	0.1	0.94	0.03	4.3	0.2	0.95	0.05	194	3	5.0	0.2	0.8	0.0
35	Cationic NFC	5	128.4	2.4	9.1	0.44	70.5	3.95	0.95	0.05	7.1	0.33	0.92	0.04	4.6	0.2	1.04	0.03	0.66	0.02	1.00	0.03	3.9	0.3	0.93	0.07	4.2	0.4	0.95	0.09	195	6	6.1	0.3	1.0	0.1
36		10	130.5	1.5	9.9	0.77	76.0	5.93	1.02	0.07	8.0	0.42	1.04	0.05	5.2	0.2	1.17	0.04	0.68	0.01	1.04	0.01	3.6	0.4	0.86	0.10	4.2	0.2	0.92	0.03	192	3	5.3	0.2	0.9	0.0
37		20	126.7	0.7	10.3	0.38	81.6	3.03	1.10	0.04	8.0	0.24	1.04	0.03	5.4	0.2	1.22	0.04	0.70	0.01	1.06	0.02	3.8	0.2	0.92	0.05	4.2	0.2	0.95	0.04	181	4	4.7	0.2	0.8	0.0
38		50	129.3	1.0	10.6	0.24	81.6	1.86	1.10	0.03	8.3	0.34	1.07	0.04	5.4	0.1	1.21	0.02	0.70	0.01	1.06	0.01	3.9	0.1	0.92	0.03	4.2	0.1	0.94	0.03	184	3	4.6	0.2	0.8	0.0
39	Cationic NFC+PLA (50% + 50%)	5	128.9	1.8	9.5	0.14	73.9	1.12	1.00	0.02	7.4	0.32	0.96	0.04	4.8	0.2	1.09	0.04	0.67	0.01	1.02	0.02	3.9	0.2	0.94	0.05	4.4	0.2	0.98	0.04	192	5	5.9	0.3	1.0	0.1
40	no polymer	0	129.3	1.5	9.7	0.33	74.7	2.56	1.00	0.00	7.9	0.32	1.00	0.00	4.8	0.1	1.00	0.00	0.68	0.02	1.00	0.00	3.9	0.1	1.00	0.00	4.4	0.2	1.00	0.00	190	5	6.1	0.3	1.0	0.0
41	Cationic NFC + PLA (50% + 50%)	10	131.0	1.3	9.3	0.55	70.9	3.84	0.95	0.05	7.6	0.51	0.96	0.06	4.5	0.2	0.95	0.03	0.66	0.02	0.97	0.02	3.9	0.3	1.00	0.07	4.3	0.2	0.97	0.05	198	5	6.6	0.4	1.1	0.1
42		20	131.7	1.4	9.9	0.82	75.3	6.23	1.01	0.08	7.9	0.25	1.00	0.03	5.2	0.1	1.09	0.03	0.70	0.01	1.02	0.02	3.6	0.3	0.90	0.08	4.2	0.2	0.95	0.04	189	4	5.9	0.6	1.0	0.1
43		50	130.7	0.7	10.5	0.55	80.1	4.20	1.07	0.05	8.4	0.26	1.06	0.03	5.2	0.1	1.09	0.02	0.70	0.01	1.02	0.01	3.8	0.3	0.95	0.06	4.3	0.2	0.97	0.04	187	3	4.8	0.2	0.8	0.1
44		50	130.9	1.4	11.4	0.63	87.1	4.78	1.17	0.07	8.6	0.24	1.09	0.03	6.0	0.2	1.25	0.04	0.71	0.01	1.05	0.01	3.7	0.3	0.95	0.06	4.2	0.2	0.97	0.04	183	3	4.8	0.1	0.9	0.2
45	GPAM	5	130.5	1.1	10.8	0.45	82.4	3.48	1.10	0.05	9.1	0.25	1.15	0.03	4.8	0.1	1.00	0.02	0.68	0.02	0.99	0.03	4.3	0.2	1.09	0.06	4.8	0.1	1.09	0.03	195	7	6.9	0.6	1.1	0.1
46		10	130.6	0.8	11.1	0.47	85.0	3.57	1.14	0.05	9.5	0.33	1.20	0.04	4.7	0.2	0.98	0.05	0.68	0.02	1.00	0.02	4.4	0.1	1.13	0.03	4.9	0.1	1.12	0.03	194	6	6.3	0.4	1.0	0.1
47		20	130.6	1.6	12.1	0.78	92.4	5.94	1.25	0.07	10.0	0.55	1.26	0.07	5.2	0.1	1.09	0.03	0.67	0.02	0.99	0.03	4.3	0.3	1.09	0.07	4.8	0.2	1.09	0.06	195	6	5.4	0.6	0.9	0.1
48	no polymer	0	131.3	1.3	9.2	0.39	69.7	2.98	1.00	0.00	7.5	0.48	1.00	0.00	4.1	0.2	1.00	0.00	0.65	0.02	1.00	0.00	4.3	0.2	1.00	0.00	4.5	0.3	1.00	0.00	200	9	6.0	0.4	1.0	0.0
49	GPAM	50	132.3	0.9	11.8	0.18	89.3	1.38	1.28	0.02	9.8	0.45	1.30	0.06	4.8	0.1	1.17	0.04	0.67	0.01	1.03	0.01	4.5	0.1	1.04	0.03	4.8	0.2	1.06	0.05	196	3	4.8	0.2	0.8	0.0
50	CPAM 2 (10 mol-% / SV0.5% 72 mPas)	5	133.4	1.3	10.2	0.31	76.4	2.33	1.10	0.04	8.0	0.33	1.07	0.04	4.8	0.1	1.18	0.03	0.69	0.01	1.06	0.01	3.9	0.2	0.91	0.04	4.3	0.2	0.94	0.05	193	3	5.3	0.2	0.9	0.0
51		10	130.6	0.8	10.3	0.18	78.6	1.36	1.13	0.02	8.1	0.38	1.08	0.05	5.0	0.1	1.22	0.02	0.69	0.01	1.06	0.01	3.9	0.2	0.92	0.04	4.3	0.2	0.95	0.05	189	2	5.2	0.2	0.9	0.0
52		20	133.6	1.6	10.4	0.36	78.2	2.70	1.12	0.04	8.4	0.16	1.13	0.02	4.9	0.2	1.19	0.04	0.68	0.01	1.04	0.02	4.0	0.2	0.94	0.03	4.3	0.2	0.94	0.05	197	4	4.9	0.2	0.8	0.0
53		50	128.6	1.1	9.7	0.44	75.3	3.41	1.08	0.05	8.0	0.26	1.09	0.04	4.8	0.1	1.18	0.03	0.69	0.01	1.06	0.02	3.9	0.1	0.90	0.03	4.3	0.1	0.94	0.03	187	4	4.7	0.2	0.8	0.0
54	CPAM 3 (6 mol-% / SV 3.4 mPas)	5	129.0	1.3	9.3	0.24	71.7	3.90	1.03	0.03	7.8	0.30	1.04	0.04	4.6	0.1	1.12	0.03	0.66	0.01	1.01	0.02	3.7	0.2	0.87	0.06	4.3	0.2	0.95	0.03	196	5	6.0	0.3	1.0	0.1
55		10	130.1	1.8	9.7	0.48	74.7	3.65	1.07	0.05	7.6	0.58	1.02	0.08	4.8	0.2	1.17	0.04	0.67	0.01	1.03	0.02	3.8	0.3	0.88	0.06	4.1	0.3	0.90	0.07	194	4	5.5	0.2	0.9	0.0
56		20	129.2	1.6	9.8	0.87	75.7	6.74	1.09	0.10	7.2	0.80	0.96	0.11	4.9	0.2	1.17	0.04	0.67	0.02	1.03	0.03	3.6	0.4	0.83	0.09	3.8	0.4	0.83	0.08	192	5	5.1	0.2	0.9	0.0
57		50	127.0	1.8	8.6	0.50	67.9	3.93	0.97	0.05	6.9	0.45	0.92	0.06	4.6	0.2	1.17	0.04	0.65	0.01	1.00	0.02	3.1	0.2	0.72	0.04	3.8	0.3	0.84	0.07	194	4	4.8	0.2	0.8	0.0

Appendix 6/7

Test	Additive/polymer		Measurements from handsheets (average of eight sheets)																															
			Grammage		Tensile strength										Modulus of elasticity				Density				Breakage strain								Thickness		Beta formation			
	quality	dosage	(RH 50 %)		Tensile strength		Tensile index		Norm. tensile index		Tensile strength		Norm. tensile strength		RH 50%				RH 50%				RH 50 %				RH 80 %				RH 50 %		RH 50%			
					RH 50%		RH 50%		RH 50%		RH 80%		RH 80%		measured		normalized		measured		normalized		measured		normalized		measured		normalized				measured		normalized	
		[kg/dry t]	[g/m^2]	S.D.	[kN/m]	S.D.	[Nm/g]	S.D.	TI/TI$_{ref}$	S.D.	[kN/m]	S.D.	TS/TS$_{ref}$	S.D.	[Gpa]	S.D.		S.D.	[g/cm^3]	S.D.		S.D.	[%]	S.D.	BS/BS$_{ref}$	S.D.	[%]	S.D.	BS/BS$_{ref}$	S.D.	[µm]	S.D.		2*S.D.		S.D.
58	no polymer	0	131.7	1.7	9.5	0.56	72.1	4.24	1.00	0.00	7.8	0.32	1.00	0.00	4.2	0.2	1.00	0.00	0.66	0.01	1.00	0.00	4.2	0.4	1.00	0.00	4.7	0.1	1.00	0.00	198	4	6.1	0.5	1.0	0.0
59	CPAM 4 (2 mol-% / SV 3.4 mPas)	5	129.4	1.9	9.1	0.22	70.5	1.70	0.98	0.03	7.9	0.32	1.01	0.04	4.1	0.1	0.99	0.03	0.67	0.02	1.00	0.03	4.1	0.2	0.97	0.04	4.7	0.3	1.01	0.07	194	6	7.5	0.4	1.2	0.1
60		10	129.2	1.2	9.4	0.62	72.7	4.81	1.01	0.07	7.6	0.41	1.11	0.03	4.5	0.2	1.08	0.06	0.66	0.02	0.99	0.03	3.9	0.4	0.94	0.09	4.5	0.3	0.97	0.03	197	7	7.5	0.3	1.2	0.1
61		20	131.0	1.4	9.1	0.99	69.1	7.56	0.95	0.11	7.7	0.62	0.99	0.08	4.3	0.2	1.03	0.04	0.66	0.02	0.99	0.03	3.7	0.5	0.89	0.11	4.5	0.2	0.96	0.04	199	6	7.7	0.4	1.3	0.1
62		50	125.9	1.2	8.6	0.58	68.2	4.62	0.95	0.07	7.0	0.48	0.90	0.06	4.5	0.1	1.07	0.03	0.66	0.01	0.99	0.02	3.6	0.3	0.86	0.06	4.1	0.4	0.88	0.07	191	5	7.3	0.4	1.2	0.1
63	Cationic guar gum	5	130.3	1.0	9.8	0.70	75.4	5.39	1.05	0.07	7.9	0.41	1.00	0.06	5.0	0.2	1.19	0.04	0.69	0.01	1.04	0.01	3.9	0.4	0.93	0.10	4.3	0.3	0.91	0.06	190	3	5.2	0.2	0.9	0.0
64		10	131.6	1.0	9.9	0.46	74.9	3.52	1.04	0.05	7.9	0.18	1.02	0.02	5.0	0.1	1.19	0.01	0.69	0.01	1.04	0.01	3.7	0.3	0.88	0.07	4.3	0.1	0.91	0.02	192	3	4.9	0.2	0.8	0.0
65		20	132.9	1.1	10.3	0.38	77.6	2.85	1.08	0.04	8.1	0.36	1.03	0.05	4.9	0.1	1.18	0.03	0.69	0.01	1.04	0.01	4.0	0.1	0.95	0.02	4.2	0.2	0.91	0.04	193	2	4.6	0.2	0.8	0.0
66		50	130.6	1.7	10.0	0.60	76.8	4.57	1.07	0.05	8.2	0.31	1.05	0.04	5.2	0.1	1.25	0.03	0.69	0.01	1.03	0.01	3.6	0.4	0.85	0.09	4.3	0.2	0.91	0.04	190	3	4.4	0.2	0.7	0.0
67	PAAE low ECH	5	130.6	1.2	9.3	0.39	71.3	3.00	0.99	0.04	7.8	0.35	1.00	0.04	4.9	0.1	1.17	0.03	0.67	0.02	1.01	0.02	3.6	0.3	0.86	0.06	4.4	0.3	0.95	0.05	195	5	6.9	0.3	1.1	0.1
68	no polymer	0	128.8	2.7	9.2	0.30	71.3	2.35	1.00	0.00	7.3	0.39	1.00	0.00	4.2	0.5	1.00	0.00	0.68	0.01	1.00	0.00	4.2	0.7	1.00	0.00	4.7	0.7	1.00	0.00	190	4	6.0	0.4	1.0	0.0
69	PAAE low ECH	10	130.6	1.4	9.9	0.37	75.6	2.80	1.06	0.04	8.3	0.22	1.14	0.03	4.6	0.1	1.09	0.03	0.66	0.01	0.97	0.02	4.0	0.1	0.88	0.02	4.7	0.1	1.00	0.03	200	10	6.3	0.4	1.1	0.1
70		20	130.8	0.8	10.3	0.38	79.0	2.90	1.11	0.04	8.5	0.42	1.15	0.06	5.1	0.1	1.20	0.03	0.69	0.02	1.02	0.03	3.9	0.2	0.85	0.04	4.5	0.3	0.96	0.06	187	6	5.6	0.2	0.9	0.0
71		50	128.6	1.2	9.5	0.34	74.1	2.61	1.04	0.04	8.3	0.69	1.13	0.09	5.0	0.1	1.18	0.02	0.68	0.01	1.01	0.02	3.6	0.3	0.79	0.06	4.4	0.1	0.95	0.02	188	4	5.7	0.5	0.9	0.1
72	CPAM 1 (10 mol-% / SV0.5% 10 mPas)	5	129.9	1.7	10.1	0.48	78.0	3.68	1.09	0.05	8.3	0.27	1.14	0.04	4.6	0.2	1.08	0.05	0.66	0.01	0.97	0.02	4.1	0.2	0.90	0.04	4.6	0.1	0.98	0.03	198	5	5.8	0.3	1.0	0.1
73		10	129.2	1.6	10.6	0.43	82.0	3.35	1.15	0.06	8.6	0.32	1.16	0.06	4.8	0.2	1.14	0.03	0.67	0.01	0.98	0.02	4.1	0.2	0.90	0.03	4.6	0.2	0.98	0.05	194	4	5.6	0.5	1.0	0.1
74		20	131.4	2.3	10.8	0.52	82.0	3.98	1.15	0.07	9.2	0.25	1.26	0.03	5.0	0.1	1.18	0.02	0.68	0.01	0.99	0.02	4.0	0.2	0.87	0.05	4.6	0.1	0.98	0.02	193	5	5.5	0.4	0.9	0.1
75		50	127.7	1.5	10.6	0.45	83.0	3.26	1.15	0.05	8.7	0.30	1.18	0.04	5.0	0.2	1.19	0.04	0.68	0.01	1.00	0.01	3.9	0.2	0.85	0.05	4.5	0.2	0.97	0.05	188	3	5.4	0.2	0.9	0.1
76	GPAM	100	129.1	1.3	11.4	0.56	88.5	4.33	1.08	0.44	9.7	0.29	1.32	0.04	4.9	0.2	1.16	0.06	0.67	0.01	0.98	0.01	4.0	0.4	0.88	0.08	4.7	0.2	1.01	0.04	194	2	5.0	0.1	0.8	0.0
77	no polymer	0	129.9	1.8	8.7	0.40	66.6	3.06	1.00	0.00	7.1	0.26	1.00	0.00	4.2	0.2	1.00	0.00	0.67	0.01	1.00	0.00	4.0	0.2	1.00	0.00	4.5	0.2	1.00	0.00	194	4	6.0	0.4	1.0	0.0
78	GPAM + CMC HMW (50% + 50%)	5	130.2	1.4	10.0	0.41	76.7	3.12	1.15	0.04	8.5	0.43	1.20	0.06	4.3	0.2	1.01	0.04	0.67	0.01	1.00	0.01	4.4	0.2	1.12	0.05	5.0	0.3	1.11	0.06	194	3	5.4	0.2	0.9	0.0
79		10	130.4	1.6	10.5	0.58	80.4	4.46	1.21	0.06	9.2	0.62	1.29	0.09	4.4	0.2	1.04	0.04	0.67	0.01	1.00	0.02	4.5	0.2	1.14	0.06	5.0	0.2	1.12	0.05	196	5	5.3	0.2	0.9	0.0
80		20	134.0	1.5	11.1	0.23	82.8	1.74	1.24	0.04	9.6	0.40	1.35	0.06	4.3	0.2	1.02	0.04	0.68	0.01	1.01	0.01	5.0	0.3	1.27	0.08	5.4	0.2	1.21	0.04	198	3	5.8	0.3	1.0	0.1
81		50	133.8	2.0	10.8	0.57	80.7	4.23	1.21	0.06	9.6	0.35	1.35	0.05	3.7	0.3	0.88	0.06	0.65	0.03	0.97	0.04	5.5	0.6	1.38	0.15	6.0	0.4	1.35	0.10	204	9	7.0	0.4	1.2	0.1
82		100	135.6	1.5	10.4	0.86	76.7	6.35	1.15	0.10	9.3	0.43	1.32	0.06	3.8	0.3	0.90	0.07	0.67	0.03	1.00	0.05	5.0	0.5	1.27	0.13	5.9	0.6	1.31	0.13	203	10	9.3	1.8	1.4	0.4
83	PAH + HA (20% + 80%)	5	129.1	1.1	9.5	0.37	73.8	2.87	1.11	0.04	7.8	0.27	1.11	0.04	4.3	0.2	1.02	0.05	0.63	0.01	0.95	0.02	3.9	0.2	0.99	0.04	4.4	0.2	0.99	0.04	204	4	6.9	0.6	1.2	0.1
84		10	130.2	2.9	10.7	0.44	81.8	3.39	1.23	0.06	8.6	0.23	1.22	0.03	4.8	0.2	1.14	0.04	0.67	0.03	1.00	0.04	4.1	0.2	1.04	0.04	4.6	0.2	1.03	0.04	192	10	6.0	0.4	1.0	0.1
85		20	128.8	1.5	10.5	0.45	81.7	3.50	1.23	0.05	9.0	0.39	1.27	0.06	4.9	0.2	1.16	0.04	0.66	0.01	0.99	0.01	3.7	0.2	0.95	0.04	4.7	0.2	1.05	0.03	195	3	5.6	0.3	0.9	0.1

Appendix 7/7

Test	Additive/polymer		Measurements from handsheets (average of eight sheets)																															
			Grammage		Tensile strength										Modulus of elasticity				Density				Breakage strain								Thickness		Beta formation			
	quality	dosage	(RH 50 %)		Tensile strength RH 50%		Tensile index RH 50%		Norm. tensile index RH 50%		Tensile strength RH 80%		Norm. tensile strength RH 80%		RH 50%				RH 50%				RH 50 %				RH 80 %				RH 50 %		RH 50%			
															measured		normalized		measured		normalized		measured		normalized		measured		normalized				measured		normalized	
		[kg/dry t]	[g/m^2]	S.D.	[kN/m]	S.D.	[Nm/g]	S.D.	TI/TI$_{ref}$	S.D.	[kN/m]	S.D.	TS/TS$_{ref}$	S.D.	[Gpa]	S.D.		S.D.	[g/cm^3]	S.D.		S.D.	[%]	S.D.	BS/BS$_{ref}$	S.D.	[%]	S.D.	BS/BS$_{ref}$	S.D.	[µm]	S.D.		2*S.D.		S.D.
86	no polymer	0	131.5	1.5	9.4	0.39	71.4	3.00	1.00	0.00	7.4	0.33	1.00	0.00	4.3	0.2	1.00	0.00	0.66	0.01	1.00	0.00	4.2	0.2	1.00	0.00	4.5	0.3	1.00	0.00	198	4	6.5	0.3	1.0	0.0
87	PAH + HA (20% + 80%)	50	129.6	1.6	10.8	0.29	83.3	2.25	1.17	0.03	9.7	0.57	1.30	0.08	4.8	0.1	1.11	0.03	0.66	0.01	0.99	0.02	3.7	0.2	0.89	0.04	4.8	0.3	1.08	0.07	195	5	6.0	0.2	0.9	0.0
89	Chitosan HMW in 0.24% adipic acid	20	126.8	1.0	8.2	0.55	64.5	4.30	0.90	0.06	6.8	0.39	0.92	0.05	4.1	0.2	0.96	0.05	0.63	0.02	0.95	0.03	3.7	0.3	0.88	0.07	4.2	0.2	0.95	0.05	201	8	8.8	0.4	1.4	0.1
88	no polymer	0	130.1	1.0	9.6	0.50	73.5	3.88	1.00	0.00	7.7	0.25	1.00	0.00	5.2	0.2	1.00	0.00	0.73	0.01	1.00	0.00	3.8	0.2	1.00	0.00	4.2	0.2	1.00	0.00	178	4	6.3	0.3	1.0	0.0
90	Cationic starch	50	130.3	0.8	12.1	0.50	92.7	3.80	1.26	0.05	10.0	0.27	1.31	0.03	5.5	0.2	1.06	0.04	0.76	0.01	1.04	0.01	4.3	0.1	1.14	0.03	4.8	0.2	1.15	0.04	171	2	5.0	0.2	0.8	0.0
91	GPAM	50	132.0	1.4	12.1	0.42	91.8	3.13	1.25	0.04	10.4	0.42	1.36	0.06	5.8	0.1	1.11	0.02	0.73	0.01	1.00	0.01	3.9	0.2	1.04	0.05	4.7	0.2	1.14	0.04	180	3	5.7	0.5	0.9	0.1
92	GPAM + CMC HMW (50% + 50%)	50	130.0	1.2	12.0	0.38	92.0	2.95	1.25	0.04	10.0	0.39	1.31	0.05	6.3	0.1	1.20	0.02	0.76	0.01	1.03	0.02	3.8	0.2	1.02	0.06	4.8	0.2	1.15	0.05	172	3	7.1	0.3	1.1	0.1
93	no polymer	0	129.2	0.9	9.8	0.35	76.1	2.73	1.00	0.00	7.76	0.41	1.00	0.00	5.5	0.2	1.00	0.00	0.74	0.02	1.00	0.00	3.7	0.2	1.00	0.00	4.0	0.2	1.00	0.00	176	3	6.4	0.4	1.0	0.0
94	GPAM + CMC HMW (25% + 75%)	5	129.8	1.2	10.6	0.50	81.5	3.86	1.07	0.05	9.04	0.24	1.17	0.03	5.7	0.2	1.03	0.03	0.74	0.01	1.01	0.02	3.6	0.2	1.00	0.05	4.3	0.2	1.06	0.08	176	3	5.5	0.2	0.9	0.0
95		10	132.0	1.5	11.5	0.32	86.9	2.44	1.14	0.03	9.78	0.30	1.26	0.04	6.0	0.2	1.09	0.03	0.75	0.01	1.03	0.01	3.7	0.2	1.02	0.04	4.5	0.2	1.12	0.05	175	3	5.5	0.5	0.9	0.1
96		20	129.1	1.3	11.4	0.69	88.3	5.33	1.16	0.07	9.92	0.33	1.28	0.04	5.9	0.1	1.07	0.01	0.75	0.01	1.02	0.02	3.7	0.3	1.02	0.09	4.5	0.3	1.13	0.06	172	3	5.4	0.3	0.8	0.1
97		50	131.5	1.4	11.8	0.58	89.8	4.44	1.18	0.06	10.36	0.31	1.34	0.04	6.0	0.2	1.09	0.04	0.76	0.01	1.04	0.01	3.6	0.3	0.99	0.08	4.6	0.1	1.14	0.03	173	3	6.3	0.4	1.0	0.1
98	GPAM + CMC HMW (75% + 25%)	5	129.2	0.8	11.1	0.75	85.8	5.84	1.13	0.08	9.48	0.28	1.22	0.04	5.7	0.1	1.04	0.02	0.73	0.01	1.00	0.01	3.8	0.4	1.03	0.11	4.6	0.2	1.15	0.04	176	3	5.4	0.3	0.9	0.1
99		10	131.6	1.5	11.4	0.42	86.6	3.20	1.14	0.05	10.09	0.30	1.30	0.04	5.7	0.1	1.08	0.02	0.74	0.01	1.01	0.02	3.8	0.3	1.03	0.07	4.7	0.1	1.19	0.02	178	4	6.0	0.3	0.9	0.0
100		20	134.4	1.9	11.8	0.46	86.6	3.20	1.15	0.04	10.04	0.44	1.29	0.06	5.6	0.2	1.08	0.04	0.74	0.01	1.01	0.01	3.9	0.3	1.07	0.07	4.7	0.2	1.19	0.06	181	3	7.0	0.2	1.1	0.0
101		50	131.3	0.8	11.1	0.62	84.8	4.69	1.11	0.06	9.88	0.41	1.27	0.05	5.8	0.2	1.04	0.03	0.74	0.02	1.01	0.03	3.7	0.3	1.01	0.07	4.8	0.2	1.21	0.06	178	5	9.2	0.9	1.4	0.2
102	no polymer	0	129.2	1.0	9.2	0.39	71.1	3.03	1.00	0.00	7.42	0.37	1.00	0.00	5.4	0.1	1.00	0.00	0.74	0.01	1.00	0.00	3.5	0.2	1.00	0.00	4.0	0.2	1.00	0.00	175	2	6.0	0.3	1.0	0.0
103	GPAM + CMC LMW (25% + 75%)	5	129.7	1.6	10.4	0.42	80.6	3.26	1.05	0.04	8.47	0.29	1.14	0.04	5.4	0.1	1.01	0.03	0.74	0.01	1.00	0.02	4.0	0.2	1.15	0.06	4.5	0.2	1.12	0.05	175	4	5.4	0.2	0.9	0.0
104		10	131.2	1.2	10.8	0.50	82.1	3.81	1.07	0.05	9.50	0.31	1.28	0.04	5.5	0.2	1.03	0.03	0.73	0.01	0.99	0.01	3.9	0.3	1.11	0.07	4.6	0.1	1.15	0.01	179	3	5.6	0.2	0.9	0.0
105		20	130.9	2.0	11.6	0.69	88.8	5.24	1.16	0.07	10.06	0.39	1.35	0.05	5.7	0.3	1.05	0.05	0.74	0.01	1.01	0.02	4.0	0.2	1.16	0.06	4.7	0.2	1.17	0.04	176	3	5.8	0.3	1.0	0.1
106		50	131.2	1.4	11.9	0.61	90.7	4.66	1.19	0.06	10.65	0.36	1.43	0.05	5.7	0.2	1.07	0.03	0.74	0.01	1.00	0.01	3.9	0.2	1.13	0.05	4.8	0.2	1.18	0.04	177	3	6.0	0.4	1.0	0.1
107	CPAM 2 + CMC LMW (25% + 75%)	5	128.9	2.0	10.5	0.49	81.5	3.78	1.07	0.04	8.35	0.50	1.14	0.07	5.4	0.1	1.00	0.02	0.73	0.01	0.99	0.01	4.0	0.3	1.14	0.07	4.2	0.2	1.05	0.05	177	3	5.5	0.2	0.9	0.0
108		10	126.7	1.4	10.7	0.38	84.1	3.03	1.10	0.04	8.66	0.24	1.17	0.03	5.4	0.1	1.01	0.03	0.73	0.01	0.99	0.01	3.9	0.1	1.13	0.04	4.4	0.2	1.10	0.05	173	3	5.1	0.3	0.9	0.1
109		20	131.4	1.0	11.0	0.59	83.7	4.46	1.10	0.06	9.30	0.40	1.25	0.05	5.3	0.1	0.99	0.02	0.73	0.01	0.98	0.01	3.9	0.3	1.11	0.08	4.5	0.2	1.11	0.05	181	2	5.0	0.3	0.8	0.1
110		50	131.1	1.8	11.4	0.69	87.1	5.23	1.14	0.07	9.63	0.43	1.30	0.06	5.5	0.1	1.03	0.03	0.75	0.02	1.01	0.02	3.9	0.2	1.13	0.06	4.5	0.2	1.12	0.06	177	5	4.9	0.2	0.8	0.0